

Compounds with non-linear optical properties

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Abstract

A polymer having non-linear optical properties, comprising a polymeric backbone a) (hereinafter defined as polymer backbone a) and at least one chromophore b) (hereinafter defined as chromophore b) attached thereto by means of a bridging moiety (hereinafter defined as bridging group c); so constituted that the chain of linking atoms (hereinafter defined as chain d) thereof does not contain an ester linkage. The polymeric backbone (a) is e.g. styrene-maleic anhydride, and the chromophore (b) may have an amino group.

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(54) Compounds with non-linear optical properties

(57) A polymer having non-linear optical properties, comprising a polymeric backbone a) (hereinafter defined as polymer backbone a) and at least one chromophore b) (hereinafter defined as chromophore b) attached thereto by means of a bridging moiety (hereinafter defined as bridging group c); so constituted that the chain of linking atoms (hereinafter defined as chain d) thereof does not contain an ester linkage. The polymeric backbone (a) is e.g. styrene-maleic anhydride, and the chromophore (b) may have an amino group.

COMPOUNDS WITH NON-LINEAR OPTICAL PROPERTIES

The invention relates to linear polymeric products having an imide-, isoimide- or amide-bound chromophore with non-linear optical properties, to their preparation and to their use, in particular for integrated optical electrooptical, photorefractive or holographic devices, such as modulators, switches, directional couplers, amplifiers, wave guides and sensors, as well as frequency convertors, especially for frequency doubling.

According to the invention, there is provided a polymer having non-linear optical properties, comprising a polymeric backbone a) (hereinafter defined as polymer backbone a) and at least one chromophore b) (hereinafter defined as chromophore b) attached thereto by means of a bridging moiety (hereinafter defined as bridging group c); so constituted that the chain of linking atoms (hereinafter defined as chain d) thereof does not contain an ester linkage.

Preferably the chain d) does not contain a urea group (-NH-CO-NH-).

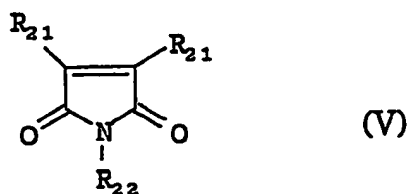
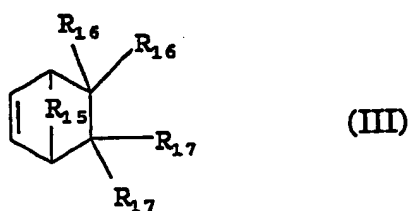
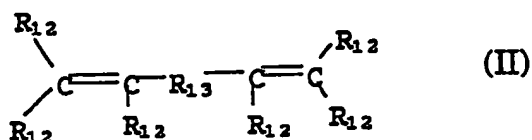
Preferably the bridging group c) contains an amide, isoimide or imide group, provided the chain d) does not contain an ester-amide group.

Preferably the bridging group c) contains an amino alkyl imido grouping, the amino being bound to the chromophore and the imido group being bound to the polymer chain.

Preferably the glass transition temperature (T_g) of a polymer according to the invention is from 120-250°C, more preferably 135-210°C.

Preferably the basis polymer for forming the polymer backbone a) (hereinafter defined as the "basis" polymer) is a homo-, co- or ter-polymer derived from monomeric compounds having one or more groups capable of condensation and/or polymerization.

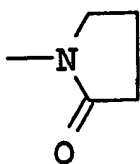
Such monomeric compounds are preferably selected from aliphatic or cyclic anhydrides or imides, for example, maleic anhydride, maleic acid imide, methacrylic acid anhydride, itaconic acid anhydride or a citraconic acid anhydride which, if copolymers form, react with vinylic compounds such as thiophene, dihydrofurane, dihydropyrane, cyclohexene, indole and N-alkylindole compounds of the formula



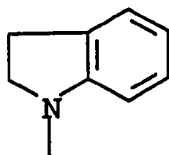
in which

R_{10} , is selected from hydrogen, chloro and C_{1-6} alkyl; and

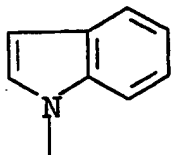
R_{10a} is selected from hydrogen, chloro, C_{1-6} alkyl, phenyl, C_{1-6} alkoxy, C_{1-6} alkyl carbonyloxy, C_{1-6} alkoxy-methyl, C_{1-5} alkylcarbonyloxymethyl, C_{1-4} alkyloxy-carbonyl and a group of formulae a) to f)



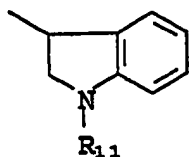
(a)



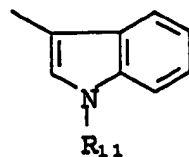
(b)



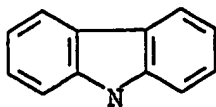
(c)



(d)



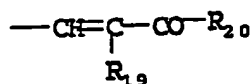
(e)



(f)

where

- R_{11} is hydrogen or C_{1-6} alkyl;
- each R_{12} independently is hydrogen or methyl;
- R_{13} is a bridging group, preferably selected from -O-, -S-, -SO₂-, -CH₂-O-, -CH₂-O-CH₂-, -CO-, -[C(R_{14})₂]- or -[Si(R_{14})₂]- where each R_{14} independently is selected from hydrogen, methyl and C_{4-6} cycloalkyl or both groups R_{14} form an omega C_{4-6} cycloalkylene group;
- R_{15} is -CH₂- ;
- each R_{16} and R_{17} independently is selected from hydrogen, -CH=CH₂, -CH=CHCH₃-, -C(CH₃)=CH₂, -CHO or -COCH₃; or
- both groups R_{16} together form a group =CH₂ or =CH-CH₃ and both groups R_{17} are hydrogen;
- or one group R_{16} and one group R_{17} form a bridge of the formula -CH₂-CH=CH- or -CO-O-CO- and the other group R_{16} and the other group R_{17} are hydrogen;
- R_{18} is hydroxy, carboxy, formyl or a group of the formula



- where R_{19} is hydrogen, methyl, ethyl or cyano; and R_{20} is hydrogen, hydroxy or C_{1-4} alkoxy;
- each R_{18a} is hydrogen, fluoro or chloro; and
- each R_{21} independently is halogen, preferably chloro or bromo or C_{1-4} alkyl and R_{22} is vinyl or alkyl.

Preferred basis polymers are the reaction products of

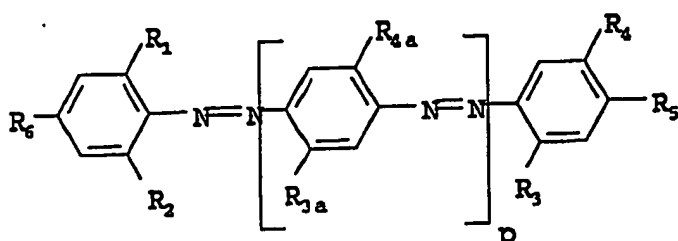
- i) an aliphatic or cyclic anhydride or imide, preferably maleic anhydride, maleic acid imide, methacrylic acid anhydride, itaconic acid anhydride or citraconic acid anhydride (hereinafter component i); with
- ii) a compound selected from thiophene, 2,3- or 3,4 dihydrofurane, 2,3-dihydropyrane,

cyclohexene, indene, indole, N-C₁₋₄alkylindole and a compound of formula I to V defined above (hereinafter component ii) .

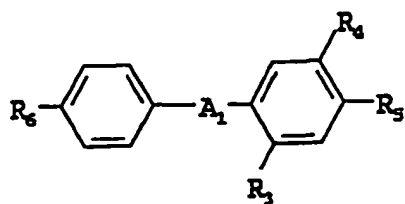
Preferably the ratio of component i) to component ii) is 10:1 to 1:10, preferably 1:1 except when component i) is a cyclic anhydride and component ii) is a compound of formula II in which case the ratio is 3:1 to 1:1 preferably 2:1.

The basis polymers for forming the polymer backbone a) are known or may be prepared by known methods from known compounds. Such known methods are those described in G. Sackmann: "Polymerisation von ungesättigten Polycarbonsäuren und ihren Derivativen": in the book "Methoden der organischen Chemie", Houben-Weyl, 4th. Ed., Vol. E 20/3, p.1234, EP 324 547 and "Synthesis and polymerization of N-(tert.butyloxy carbonyl)-maleimide and facile deprotection of polymer side chaining A-BOC groups in Polymer, 1992 vol. 33, Nr. 22, p. 4851-4856, Kwong-Duk Ahn et al: the contents of these two references are incorporated herein by reference. Examples 1-15 also illustrate how the basis polymer can be prepared. The basis polymers that are not known can easily be made by a man skilled in the art by analogous methods to those above.

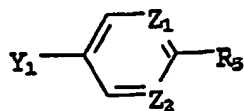
The chromophores b) with non-linear optical properties are bearing groups able for reacting with the acid derivatives (for example, an anhydride or acid chloride, for forming an imide, isoimide or amide) of the basis polymers are of formula XI-XV



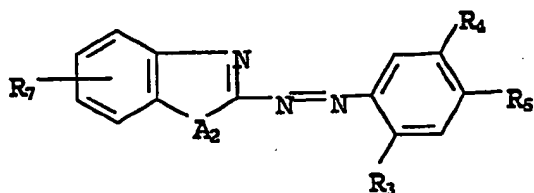
(XI)



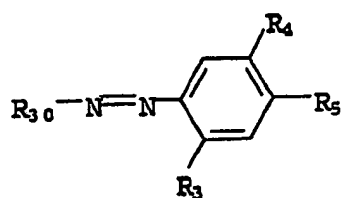
(XII)



(XIII)



(XIV)



(XV)

in which

R_1 is hydrogen, halogen, carboxyl, cyano or rhodan;

R_2 is hydrogen, halogen, cyano, carbonyl or nitro;

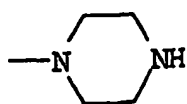
R_3 is hydrogen, methyl, ethyl, methoxy, ethoxy, amino- C_{1-2} alkyl or C_{1-2} alkylcarbonyl amino;

R_{3a} is hydrogen, methyl, ethyl, methoxy or ethoxy

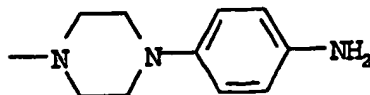
R_4 is hydrogen, methoxy or ethoxy;

R_{4a} is hydrogen, methoxy or ethoxy;

R_5 is a group of the formula $-NH_2$, $-N(R_3)-(CH_2)_n-NH_2$;

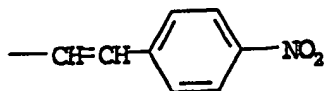


or



and when R_3 is C_{1-2} alkyl amino, R_5 may additionally be $di(C_{1-4}alkyl)$ amino;

R_6 is cyano, nitro, C_{1-2} alkylsulphonyl, aminosulphonyl, dicyanovinyl, tricyanovinyl, $di(C_{1-4}alkoxycarbonyl)$ vinyl of a group of the formula $-C(C_{1-4}alkyl)=C(CN)_2$, $-CH=CH-NO_2$, $-CH=C(CN)-CO-O-C_{1-4}alkyl$, or



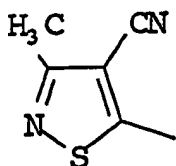
R_7 is hydrogen or nitro;

R_8 is hydrogen, $C_{1-4}alkyl$, benzyl or $C_{1-2}alkoxycarbonyloxy-C_{2-3}alkyl$;

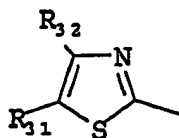
A_1 is a direct bond, $-CH=CH-$, $-N=CH-$ or $-CH=N-$;

A_2 is $-S-$ or $-O-$;

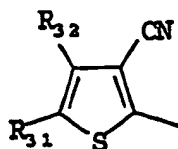
R_{30} is a group of the formula a), b) or c)



a)



b)



c)

where

R₃₁ is tricyanovinyl, -NO₂, -CHO, -CH=C(CN)₂, -CH=CH-NO₂, -CH=C(CN)-
(COOC₁₋₄alkyl)₂ or CH=C(COOC₁₋₄alkyl)₂

R₃₂ is hydrogen, chloro, C₁₋₄alkyl or phenyl;

Y₁ is nitro, formyl, cyano, C₁₋₂alkylsulphonyl, tricyanovinyl or dicyanovinyl;

-Z₁= is -N=, =CH- or =C(NO₂)-;

-Z₂= is =N-, =CH- or =C(NO₂)-;

p is 0, 1 or 2; and

n is 0 or 1 to 9

Preferably any halogen in this specification is Cl or Br, more preferably Cl.

Preferably R₁ is R₁' in which R₁' is hydrogen, chloro or bromo.

Preferably R₂ is R₂' where R₂' is hydrogen, chloro, bromo, cyano or nitro;

Preferably R₃ is R₃' where R₃' is hydrogen, methyl or C₁₋₂alkylcarbonylamino.

Preferably R_{3a} is R_{3a}' where R_{3a}' is hydrogen or methyl.

Preferably R₄ is R₄' where R₄' is hydrogen, methoxy or ethoxy.

Preferably R_{4a} is hydrogen.

Preferably R₅ is (N-C₁₋₂alkyl-N-γ-amino-C₂₋₃-alkylene)-amino, (N-benzyl-N-

γ aminopropyl)-amino or N-piperazyl.

Preferably R_6 is R_6' where R_6' is cyano, nitro, dicyanovinyl or C_{1-2} alkylsulphonyl.

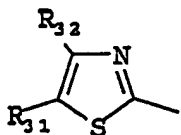
Preferably R_7 is nitro

Preferably n is n' where n' is 1, 2 or 3, more preferably n'' where n'' is 2 or 3.

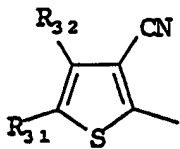
Preferably p is p' where p' is 0 or 1, more preferably 0.

Preferably A_2 is -S-.

Preferably R_{30} is R_{30}' where R_{30}' is



b)



Preferably R_{31} is R_{31}' where R_{31}' is dicyanovinyl, tricyanovinyl, formyl or di- $(C_{1-2}$ alkoxycarbonyl)vinyl.

Preferably R_{32} is R_{32}' where R_{32}' is hydrogen, methyl, chloro or phenyl.

Preferably Y_1 is Y_1' where Y_1' is nitro or cyano.

Chromophores with non-linear optical properties are known or can be prepared from

known compounds by known methods.

The compounds according to the invention can be prepared by reacting monomers having one or more polymerizable groups and/or groups capable of undergoing condensation reactions with a chromophore-bearing compound having one or more groups capable of condensation or addition.

Preferably the monomers, for producing homo- or copolymers (optionally also terpolymers) of the basis polymers contain one or two (preferably one) polymerizable groups and one group capable of condensation with the chromophore-bearing compound. Examples of such compounds are aliphatic and cyclic anhydrides and optionally amides, which when used to form as a copolymer are preferably the products of component ii defined above.

Chromophore-bearing compounds for reaction with the above mentioned polymers, preferably are compounds of formula XI to XV containing amino groups, which may be in salt form (e.g. hydrochloride, hydrosulphate or sulphate) or may also contain a protected amine group. These chromophore-bearing compounds react with the groups capable of condensing with the above mentioned polymer a) (or monomers used to form the polymers) by forming an amide or an isoimide and/or then finally cyclising to form the imide.

Groups in the basis polymer (or monomers that form the basis polymers) that can form an amide, isoimide or imide by condensation are preferably functional carboxylic acid derivatives especially carboxylic acid anhydrides and (less preferably) carboxylic acid halides. The reaction conditions to carry out such reactions are known to a man skilled in the art.

Homopolymers of basis polymers can be prepared from monomers containing a number of groups suitable for condensation and/or polymerization. Preferably however, there is one group capable of condensation and one group capable of

polymerization in each monomer. Homopolymers of polymer backbone a) preferably contain residues from acrylic acid anhydride, methacrylic acid anhydride, citraconic acid anhydride or itaconic acid anhydride.

There is a description, in some of the following Examples, of the reaction of polymer-bound cyclic carboxylic anhydrides with an appropriate chromophore-bearing compound having an amino group present (e.g. compounds of formula XI to XV) followed by cyclization (by splitting off water) using cyclization agents (e.g. acetic acid anhydride). Alternative methods are described - for example from Tetrahedron Lett. 32, 3449 (1991) by J.A. Moore et al and EP 324547. In the alternative, amides with free carboxylic acid groups (e.g. the isoimides) are described in Polymer Preprints 26 (1985) p.287-8 in an article by F.W. Harris et al "Polyimides containing oxyethylene units III. Isoimide Precursor to semicrystalline Polyamides". These products can be reacted further by known methods to give compounds according to the invention.

Preferred chromophore-bearing compounds are those containing a secondary amino group, especially a free piperazyl group. These result in amide acids, (see Examples 118-112, 127 and 128 below) having a free carboxylic acid group per chromophore group.

The polymers with non-linear optical properties according to the invention can also be prepared by reacting a polymeric cyclic carboxylic acid anhydride with isocyanate containing chromophore bearing compounds. Such a process is analagous to that described in J. Polymer Science, Part A1, 7(1969) p. 2757 by R.A. Meyers et al). The intermediate 7-membered ring structures also form a part of the present invention.

Polymers according to the invention can also be prepared by radical copolymerization of chromophore-bearing maleic acid imide (from maleic acid anhydride and a chromophore bearing an amino group) with a vinyl compound (for example component ii defined above).

Furthermore, compounds according to the invention can be prepared by reacting polymer-bound cyclic carboxylic acid imide (especially maleic acid imide) with a chromophore containing a primary hydroxy group (for example by the "Mitsunobu" reaction described in Angew. Chemie 103, (1991 p. 106-108 by I Cabrera et al).

Polymers according to the invention with a dicyanovinyl or dicyanovinyl ester group present can be prepared by the reaction of a chromophore-bearing polymer with an aromatic aldehyde group (e.g. malonic acid dinitrile or cyanomalonic acid esters). Such procedures are described in "Organikum" Organisch Chemisches Grundpraktikum, 15th Edition, VEB, Deutscher Verlag der Wissenschaften, Berlin 1977 p. 571 et seq.

The compounds of the invention also include polymers in which not every recurring unit has a chromophore group b) present.

However, it is preferred that the number of chromophores with non-linear optical properties present is as high as possible which however is kinetically difficult to achieve. Usually the maximum chromophore content is about 98% (as evidenced by Example 122) except where the chromophore is reacted with the polymerizable monomer prior to polymerization.

The molecular weight of basis polymers (without the chromophore present) of the polymers according to the invention is from 2×10^3 to 5×10^6 , more preferably 1×10^4 to 3×10^5 .

The molecular weight of such basis polymers can be regulated by known methods to a man skilled in the art, for example by regulating initiator concentration, (e.g. azoisbutyronitrile), the monomer concentration and/or the reaction temperature. The molecular weight of the basis polymers can also be controlled by known methods using regulators (e.g. a mercaptan).

Polymers according to the invention are primarily used in the form of thin films, for the formation of layers in optical or electrooptical parts in order to produce non-linear optical effects, for example for use as modulators, electrooptical switches, for changing frequency (such as frequency doubling).

The polymers show very good solubility in solvents and are easily workable (for instance, spin coating or dip coating). The glass transition temperature (T_g) of copolymers according to the invention is high, and their long term stability and their high non-linear coefficients for electrooptical and non-linear optical effects are worthy of note. Films made with polymers according to the invention show good wave guiding properties (with little damping).

Compared to compounds known to for similar use, the compounds according to the invention have the following advantages, high molecular weight (up to 5×10^6), good solubility in organic solvents, good workability and a relatively simple synthesis.

Especially to be noted is that the compounds according to the invention have a high glass transition temperature with high non-linearity, especially for compounds containing group derived from compounds of formula IV.

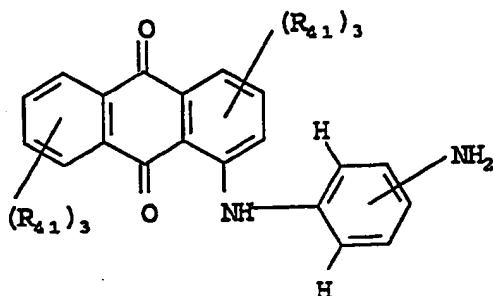
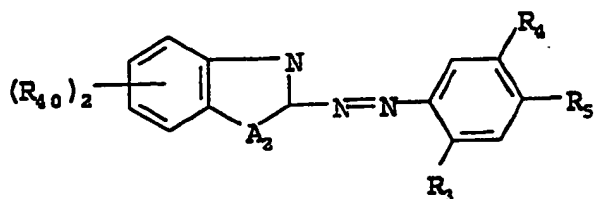
Further, films made using one or more polymers according to the invention, have good wave guide properties for laser light of differing wavelengths. Of special preference are wave guides made out of three layers, in which the uppermost and lowermost layers have lower breaking indices than those of the middle layer and that the glass transition temperature T_g of the uppermost and lowermost layers is greater than or at least the same as that of the middle layer.

Further according to the invention, there is provided an optical device comprising

- a) a top buffer being a layer of polymer a) as defined above containing no non-linear optical (NLO) chromophore, a minor amount (e.g. from 1-10%) of NLO chromophore or non-NLO chromophore;

- b) a main layer being a layer of a polymer according to the invention (i.e. containing 10-100% NLO chromophore); and
- c) a bottom buffer, being a layer of polymer a) containing no NLO chromophore, a minor amount of NLO chromophore (e.g. from 1-10%) or non-NLO chromophore.

Preferred non-linear optical chromophores (non-NLO chromophores are those of formula VI and VII



in which A_2 , R_3 , R_4 and R_5 are defined above,

each R_{40} independently is selected from hydrogen, fluoro, chloro, bromo, methyl and methoxy; and

each R_{41} independently is selected from hydrogen, chloro, bromo, amino, mono- or di C_{1-4} alkylamino C_{1-4} alkoxy and hydroxy.

Examples 109-114 describe such chromophores.

The invention will now be illustrated by the following Examples.

Unless indicated to the contrary all parts are by weight and all temperatures are in

°C.

Examples 1-6 relate to the preparation of polymer backbone a);

Examples 7-12 relate to the preparation of multifunctional compounds of component ii);

Examples 17-114 related to the preparation of chromophore;

Examples 115-204 relate to the preparation of polymers according to the invention; and

Examples 205-211 are applications examples.

T_g = glass transition temperature

Examples

α) Production of polymer chains a

Example 1

Poly-(styrene co maleic acid anhydride) is produced as follows. 10.4g (0.1mol) of styrene, 9.8g (0.1 mole) of maleic acid anhydride, 300 ml of benzene and 0.1 g (0.4 mmole) of benzoyl peroxide are added to a vessel and are stirred at room temperature until a clear solution results. Whilst stirring, the mixture is heated to boiling. The copolymer results. after 1 hour the mixture is allowed to cool and the solid polymer is separated out and dried under vacuum. This is the method described in "Praktikum der Makromolekularen Organischen Chemie", 2nd edition, page 220, by D. Braun, H. Cherdron, W. Kern and Dr. A. Hühlig Verlag, Heidelberg 1971. In this method, toluene at 70°C, or benzene is used as the solvent and azo-bis-isobutyronitrile or benzoyl peroxide as initiator.

Extremely high molecular weight poly(styrene-co-maleic acid anyhdride) can be prepared according to the method of G. Sackmann in Houben-Weyl, Methoden der Organischen Chemie E20, Part 3, 4th Edition p. 1243 et seq. H. Bartel, J. Falbe (ed.)

G. Thieme Verlag.

Exempl 2

Poly-(ethylene co maleic anhydride) is produced by the method of G. Sackmann in Houben-Weyl, Methoden der organischen Chemie, E20, Part 3, 4th edition, page 1242 et seq., by H. Bartel, J. Falbe (Eds.), G. Thieme Verlag. Toluene is used as the solvent and azo-bis-isobutyronitrile as initiator.

Analogously to the above, from appropriate reactants, poly(propen-co-maleic acid anhydride) and poly(isobutene-co-maleic acid anhydride) can be produced. Similarly, poly (α -methylstyrene-co-maleic acid anhydride) and poly(norbornadiene-co-maleic acid anhydride) can be prepared.

Example 3

Poly-(ethyl vinyl ether co maleic anhydride)

A solution of 14.71 g of maleic anhydride, 14.4 ml of ethyl vinyl ether and 123 mg of azoisobutyronitrile in 200 ml of toluene is rinsed with nitrogen for 5 minutes and the solution subsequently stirred for 1 hour at 60°. The copolymer precipitated during the reaction is filtered off, washed with 200 ml of toluene and dried at 50°/25 torr.

Example 4

Poly-(furan co maleic acid anhydride) is produced according the method described in J. Polym. Sci., Polym. Chem. Ed., 16, 1527 (1978) by N.G. Gaylord, M. Martan, A.B. Deshpande.

According to this process, the Diels-Alder product resulting from furane and maleic acid anhydride can be polymerized. Maleic anhydride and furance are reacted together in the presence of azobisisobutyronitrile. The product is prepared in anhydrous diethyl ether at 35°C and recrystallized from ethyl acetate.

Example 5

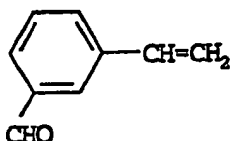
Poly-(divinyl sulphone co maleic acid anhydride) is produced according to the method of J. Macromol. Sci. Chem., A5, 219 (1971) by G.B. Butler,

Example 6

Poly-(methacrylic acid anhydride) is produced according to the method of J. Am. Chem. Soc., 80, 5464 (1958) by A. Crawshaw, G.B. Butler,

Example 7

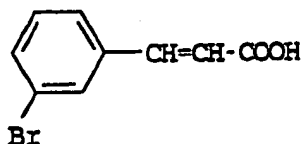
The preparation of a compound of the formula



can be prepared according to the process given of Makromol. Chem. 189, 119-127 (1988) by W. Heitz et al from m-bromobenzylaldehyde and ethylene. The melting point of the product is 121°C/28 mbar.

Example 8

The preparation of a compound of the formula

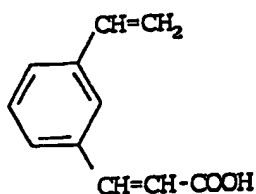


can be prepared by the Knoevenagel reaction of m-bromobenzylaldehyde and malonic

acid. The method is described in Autorenkollektiv, Organikum, Organisch-Chemisches Praktikum, VEB Deutsches Verlag der Wissenschaften, Berlin 1977, p. 572 Variante B. The melting point is 180°C.

Example 9

The preparation of a compound of the formula

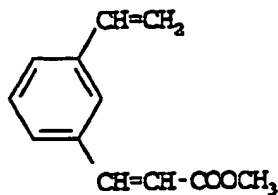


can be prepared as follows:

A reaction mixture of 63.7 g of m-bromocinnamic acid, 1.75g of tri-o-tolyl phosphine and 0.63g of palladium acetate in 280 ml of acetonitrile and 220 ml of triethylamine is placed in an autoclave and is sparged with nitrogen for 2 minutes and then pressurized to 15 bar ethylene at room temperature. With a heating rate of 2°C per minute, the temperature is brought to 125°C and is held at this temperature for 20 hours. The pressure rises to 35 bar. The reaction mixture is allowed to cool to room temperature and the filtered product is poured with a mixture of 165 ml of concentrated hydrochloric acid and 450 ml of ice-water. The resultant brown mixture is extracted three times with 400 ml of diethylether (400ml per extraction) and the combined ether phasees are filtered and extracted with two times 300mls of 20% sodium carbonate solution. The aqueous phase is slowly added to a mixture of 260ml of concentrated hydrochloric acid and 500 ml of ice-water. The resulting white product is filtered off and dried under vacuum at room temperature. Mp 152-155°C.

Example 10

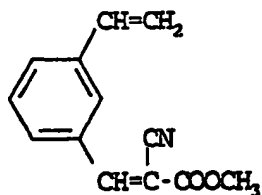
A product of the formula



can be prepared as follows: m-vinylcinnamic acid (a known compound) can be prepared by reaction with thionylchloride followed by esterification with methanol by known method (for example in "Autorenkollektiv, Organikum, Organisch-Chemisches Praktikum, VEB Deutsches Verlag der Wissenschaften, Berlin 1977 p. 505 et seq.). R_f (Kieselguhr/toluene) = 0.41.

Example 11

A product of the formula



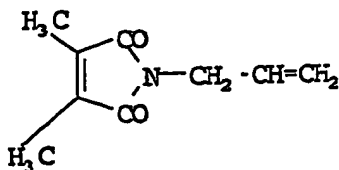
can be prepared as follows. M-vinyl- α -cyano-cinnamic acid methyl ester can be produced by the Knoevenagel reaction from m-vinylbenzaldehyde and cyanoacetic acid methyl ester according to the method of "Autorenkollektiv, Organikum, Organisch-Chemisches Praktikum, VEB Deutsches Verlag der Wissenschaften, Berlin 1977 p. 572, Variante A) as follows:

A mixture of 61g of m-vinylbenzaldehyde, 41 ml of cyanoacetic acid methyl ester, 4.1g of β -aniline, 0.5 g of hydroquinone and 5.3 ml of glacial acetic acid are mixed in 250 ml of toluene in a water distillation apparatus under reflux until no further water is removed (about 1.5 hours). After cooling, the product is extracted with 3 times 350 mls of about 4% sodium carbonate solution and once with 400 ml of water. The organic phase is diluted with 400 ml of methylene chloride and is dried over sodium sulphate. After distilling off the solvent, the product is recrystallized from toluene/hexane R_f (Kieselguhr/toluene) = 0.43

IR (KBr): 2225 cm^{-1} , m, CN; 1724 cm^{-1} , S, methylester; 1608 cm^{-1} , C=C

Example 12

A compound of the formula



can be prepared as follows. N-allyl-2,3-dimethyl maleic amide can be prepared from 2,3-dimethylmaleic acid anhydride and allylamine according to the process of D.O.S. 2,934,550 (Ciba Geigy) b.p. = 98°C/1mbar.

Example 13

Poly(maleic acid anhydride co-allyl-2,3-dimethyl maleic imide) can be prepared from a solution of 30.79g of allyl-2,3-dimethylmaleic imide, 17.36 g of maleic acid anhydride and 581 mg of azo-bisisobutyronitrile in 40ml of toluene. This is sparged with oxygen-free nitrogen for 5 minutes followed by tempering in a gas-sealed flask for 24 hours at 70°C. The reaction mixture is then diluted with 120 ml of tetrahydrofuran and is slowly added, dropwise while stirring well, to 1.9 l of

methanol. The resultant copolymer is filtered over a glass frit and dried until a constant weight results.

IR (KB+): 1701 cm^{-1} , s, C=O maleicimide; 1784 cm^{-1} , s, 1860 cm^{-1} , w, C=O anhydride. Elemental analysis C: 58.2% H: 5.2% N: 5.3% O: 31.3%.

Example 14

Poly(maleic acid anhydride-co-m-vinyl- α -cyano-cinnamic acid methylester)

A filtered solution of 1g of m-vinyl- α -cyano-cinnamic acid methylester, 460 mg of maleic acid anhydride and 15.5 mg of azo-bis-isobutyronitrile in 15ml of toluene is sparged for 3 minutes in oxygen-free nitrogen and sintered in a gas-sealed flask for 17 hours at 60°C . The resulting copolymer is filtered over a glass frit, washed with toluene and dried until a constant weight results. Parameters of the product are: U.V. (CH_2Cl_2): 302 nm, cyanocinnamic acid methylester

IR(KBr) 2225 cm^{-1} , w, CN, 1782 cm^{-1} , s, 1859 cm^{-1} , w, C=O anhydride; 1733 cm^{-1} , C=O. Methylester; 1610 cm^{-1} , m, C=C.

In a method analogous to that of Example 14, from appropriate reactants, poly(m-vinylcinnamic acid methyl ester-CO-maleic acid anhydride) can be prepared.

IR (KBr) : 1781 cm^{-1} , s, 1859 cm^{-1} , w, C=O anhydride; 1717 cm^{-1} C=O methylester; 1639 cm^{-1} , m, C=C.

Poly-(m-vinylcinnamic acid-co-citraconic acid anhydride) and poly(m-vinylcinnamic acid-co-itaconic acid anhydride) can be made from appropriate reactants analogously to the method of Example 14.

Example 15

Poly(m-formyl styrene-co-maleic acid anhydride) can be prepared from appropriate reactants analogously to the method of Example 1. The product is dissolved in dimethyl formamide and precipitates out in methanol. The product has the following parameters.

IR (KBR): 1858 cm^{-1} , w, 1780 cm^{-1} , s, C=O anhydride; 1699 cm^{-1} , s, CHO.

Example 16

p-hydroxy styrene is prepared by the method of Example 5 of D.O.S. 2,248,525. The melting point is $69-71^{\circ}\text{C}$.

Poly(p-hydroxystyrene-co-maleic acid anhydride) is made analogously to the method of Example 1 from appropriate reactants. The solvent used is 1:1 mixture of toluene/acetone and the copolymer is precipitated out in diethylether.

The product has the following parameters:

IR (KBR): 3447 cm^{-1} , b, OH, 1856 cm^{-1} , m, 1772 cm^{-1} , s, C=O anhydride.

Preparation of Chromophores**Example 17**

The preparation of 4-nitro-4'-(N-ethyl-N- β -amino ethyl)-1,1' azobenzene hydrochloride can be carried out as follows:

a) Preparation of N-ethyl-N-cyanomethylaniline

A mixture of 1051 g of N-ethyl aniline, 1060 ml of dimethylformamide, 206g of magnesium oxide and 22.5 g of potassium iodide are placed in a 10 liter sulphonating vessel. This is heated to 100°C and 569 mls of chloroacetonitrile is added dropwise over 90 minutes. This is stirred for 2 hours at 120°C and then 340 ml of acetic acid anhydride is added at 100°C whereby a brown solution results. After 30 minutes, 3200 of toluene and 3200 mls of water are added at 75°C and after cooling the reaction mixture is poured into a separating funnel. The aqueous phase is separated off and is extracted twice with 500 ml of toluene. The combined organic phase is then washed with 500 ml of water, dried overnight over magnesium sulphate and the solvent is then removed with a rotary evaporator. 1485g of product results as a brown oil, that can be used as such further.

b) N-ethyl-N-(β -aminoethyl)aniline can be prepared as follows:

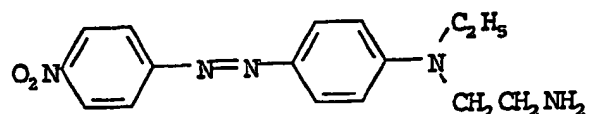
A mixture of 3000 ml of isopropanol, 350 ml of liquid ammonia, 742 g of N-ethyl-N-cyanomethyl aniline as well as 74g of a nickel catalyst H 1-50, commercially available from BASF. This mixture is hydrated at 90°C and 10 bars pressure for 2.5 hours. The amount of hydrogen used is 190 liters. A light brown solution results, that is concentrated at 50°C and 500 mbar (initially followed by 20 mbar) in a rotary evaporator. 730 g of a light brown oil result. Distillation is carried out at 96-98°C and 0.02 mbar. 587 g (84.1% of theory) of the product results as a colorless fluid.

c) Coupling with 4-nitroaniline

1650 ml of water, 528 g of a 30% solution of hydrochloric acid and 174 g of 4-nitroaniline (95.5%) are stirred in a 3 liter sulphonating vessel for 2 hours at room temperature. By cooling from outside and by the addition of 200g of ice, the reaction mixture is cooled to 0°C. 250 ml of a 33% sodium nitrite solution is added stirred for 2 hours at 0-5°C. Excess nitrite is then destroyed by the addition of amidosulfonic acid and the product is filtered through a glass funnel G1.

The filtrate is placed in a 10 liter sulphonating vessel at 0°C and a solution of 205.3g of N-ethyl-N-(β-aminoethyl)aniline and 300g of water (together with the dropwise addition of a 30% hydrochloric acid solution to give a pH value of 1) is added at 0°C. This is stirred for 2 hours at 0°C and then is warmed to room temperature overnight. 2 liters of water are then added and the pH is brought to 2 through the addition of 30% sodium hydroxide, whereby a thick precipitate results. After stirring for 2 hours, the product is filtered with a glass filter G3 under vacuum, the product is dried at 80°C and 500g of a red dyestuff results.

To purify the product, it is heated to 100°C in 200 ml of dimethylformamide and the undissolved parts are filtered off. The warm filtrate is reacted with 4000 ml of chloroform and the product is allowed to crystallize out. 258 g of a dyestuff (in hydrochloride form) of the formula



Rf value 0.43

results. Thin layer chromatography is carried out with films of POLYGRAM SIL G/UV 254 (from Machery-Nagel). The solvent is a mixture of 50 parts toluene, 20 parts of ethanol, 10 parts of triethylamine, 10 parts of dioxane and 2.5 parts of water.

Example 18

- a) Production of 2-chloro-4-nitro-4'-(N-methyl-N-γ-aminopropyl)-1,1'-azobenzene is carried out as follows:

A mixture of 4300 ml of isopropanol, 185 ml of liquid ammonia, 494 g of N-methyl-N-cyanoethyl-aniline and 50 g of nickel catalyst H1-50 from BASF is placed in a 5 l steel autoclave. The mixture is hydrogenated for 2 hours at 90° and

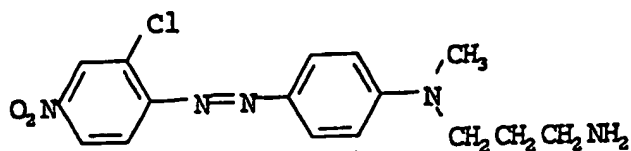
at 5 bars pressure. The hydrogen consumption here is 141 l. After filtering off the catalyst, the light brown solution is concentrated in a rotary evaporator at 45° and at 135 mbar, whereby 656.6 g of a light brown oil are obtained. Distillation at 83° and 0.015 mbar yields 479.4 g (94.7% of theory) of N-methyl-N-(γ -aminopropyl)-aniline in the form of a colorless liquid.

b) Coupling with 2-chloro-4-nitroaniline

170 g of a 95% sulphuric acid are added dropwise whilst stirring to 270 ml of ice water in a 1.5 l sulphonation flask. 96 g of 2-chloro-4-nitroaniline are added at room temperature, and stirring is effected for ca. 1 hour. The mixture is cooled to 0°, 113 g of a 33% sodium nitrite solution are added, and stirring is effected for 3 hours. Subsequently, the excess nitrite is broken down with amidosulphonic acid.

89 g of N-methyl-N-(γ -aminopropyl)-aniline (from part a) above) in 200 ml of DMF are placed in a 3.5 l sulphonation flask at 0°. The yellow-brown diazonium salt suspension is added over the course of ca. 1-2 hours using a compression pump with hose, whereby by simultaneously adding in dropwise a 30% sodium hydroxide solution, a pH value of 1.5 is maintained, and the temperature of the reaction mixture is held at constant 0-5°. Stirring is effected for 3 hours, then the pH value is set at ca. 5, filtering is effected for a further 2 hours, and the product is dried in a vacuum at ca. 60-80°, thus producing ca. 178 g of a red dyestuff.

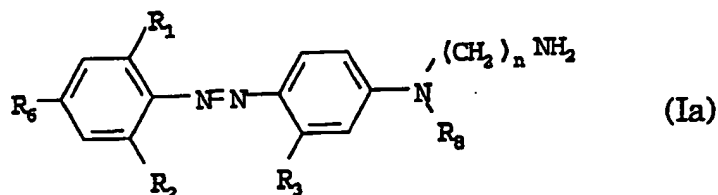
The dyestuff is purified by suspending in ca. 3-4 times 2 l of toluene in a 3.5 l sulphonation flask, respectively heating at reflux for 2 hours, and then filtering. The product is subsequently stirred at room temperature with a mixture of 2 l of methanol and 200 ml of a 10% solution of sodium hydroxide, is then filtered off and dried in a vacuum at ca. 60°. Ca. 149 g of the dyestuff of the formula



result. Rf value 0.31. Thin layer chromatography can be carried out as in Example 17.

Examples 19-56

Compounds of the formula



in which the symbols are as defined in Table 1 below can be prepared from suitable reactants analogously to the method of Example 17 (ammonium salt form) or 18 (free amine form) above.

TABLE 1

Ex. Nr.	R ₁	R ₂	R ₃	R ₆	n	R ₈	R _f
19	H	H	H	NO ₂	2	-CH ₃	0.35*(a)
20	H	H	H	do	3	do	0.31*(a)
21	Cl	Cl	H	do	3	do	0.34*(a)
22	H	-CN	H	do	3	do	0.26*(a)
23	Br	-NO ₂	H	do	3	do	0.29*(a)

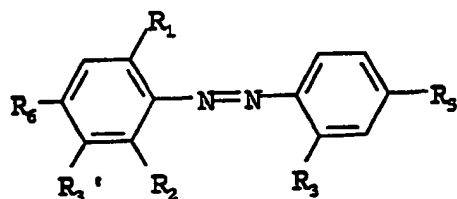
Ex. Nr.	R ₁	R ₂	R ₃	R ₆	n	R ₈	Rf
24	H	H	-CH ₃	do	3	-C ₂ H ₅	0.38*(a)
25	H	Cl	do	do	3	do	0.37*(a)
26	Cl	Cl	do	do	3	do	0.39*(a)
27	H	-CN	do	do	3	do	0.31*(a)
28	Br	-NO ₂	do	do	3	do	0.32*(a)
29	H	Cl	do	do	3	-CH ₂ C ₆ H ₅	0.49*(a)
30	-NO ₂	H	do	do	3	-C ₂ H ₅	
31	do	H	H	do	3	-CH ₃	
32	do	Cl	-CH ₃	do	3	-C ₂ H ₅	
33	H	H	H	do	3	-CH ₂ C ₆ H ₅	
34	H	Cl	H	do	3	do	
35	Cl	Cl	H	do	3	do	
36	H	-CN	H	do	3	do	
37	H	Cl	H	do	2	-C ₂ H ₅	
38	H	Cl	-CH ₃	-NO ₂	2	-C ₂ H ₅	
39	H	-CN	H	do	2	do	
40	H	H	H	-CH=C(CN) ₂	2	do	0.51(b)
41	H	H	H	-CH=C(CN) ₂	2	-CH ₃	
42	H	-NO ₂	H	-NO ₂	3	-CH ₂ C ₆ H ₅	
43	H	H	-CH ₃	do	3	do	
44	H	-CN	do	do	3	do	
45	H	-NO ₂	do	do	3	do	
46	Br	do	do	do	3	do	
47	H	H	do	-CN	3	-C ₂ H ₅	
48	H	H	do	do	3	-CH ₂ C ₆ H ₅	
49	H	H	do	-SO ₂ CH ₃	3	-C ₂ H ₅	
50	H	H	do	-CH=C(CN) ₂	3	do	0.42(b)

Ex. Nr.	R ₁	R ₂	R ₃	R ₆	n	R ₈	R _f
51	H	H	H	do	3	-CH ₃	
52	H	H	H	do	3	-CH ₂ C ₆ H ₅	
53	H	H	-CH ₃	do	3	do	
54	H	H	do	$\begin{array}{c} \text{CN} \\ \\ -\text{CH}=\text{C} \\ \\ \text{COOC}_2\text{H}_5 \end{array}$	3	-C ₂ H ₅	
55	H	H	do	$\begin{array}{c} \text{CN} \\ \\ -\text{CH}=\text{C} \\ \\ \text{COOC}_4\text{H}_9 \end{array}$	3	do	0.17(b)
56	H	H	do	-SO ₂ NH ₂	3	do	

R_f values are measured by the same thin layer chromatography method as in Example 17 to give results a). Results b) are obtained the same way except that the solvent used is 30 parts of chloroform and 10 parts of methanol.

Examples 57-70

Compounds of the formula



in which R_3' is hydrogen in Examples 57-60 and 63-70 and in Examples 61 and 62 R_3' is $-\text{CH}_3$ and the other symbols are as defined in Table 2 below, can be made from appropriate reactants by a method analogous to that of Example 17 or 18. R_3' is always hydrogen, except in Example 62, where it is methyl.

TABLE 2

Ex Nr.	R_1	R_2	R_3	R_5	R_6	Rf
57	H	H	H	n-piperazyl	$-\text{NO}_2$	0.36
58	$-\text{CN}$	H	H	do	do	0.34
59	$-\text{COOH}$	H	H	do	do	0.03
60	Cl	H	H	do	do	
61	H	H	H	$-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2)_2-\text{NH}_2$	$-\text{N}=\text{N}-$ $-\text{NO}_2$	0.40
62	$-\text{H}$	H	H	$-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2)_3-\text{NH}_2$	do	0.29
63	H	H	H	$-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2)_3\text{NH}_2$	$-\text{NO}_2$	
64	H	H	$-\text{CH}_3$	$-\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{NH}_2$	do	
65	H	H	H	$-\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{NH}_2$	$-\text{SO}_2\text{CH}_3$	
66	CN	H	H	$-\text{NH}_2$	$-\text{NO}_2$	0.79
67	H	H	H	$-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2)_3\text{NH}_2$	$-\text{CH}=\text{CH}-\text{NO}_2$	
68	H	H	CH_3	$-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2)_3\text{NH}_2$	do	

Ex Nr.	R ₁	R ₂	R ₃	R ₅	R ₆	R _f
69	H	H	CH ₃	-N(C ₂ H ₅)-(CH ₂) ₃ NH ₂	-C(CN)=C(CN) ₂	
70	H	H	H	-N(C ₂ H ₅)(CH ₂) ₃ NH ₂	do	

R_f values are measured according to the thin layer chromatography method of Example 17.

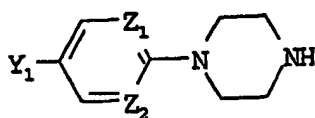
Example 71

The preparation of 5-nitro-2-piperazine-pyrimidine is carried out as follows:

A mixture of 1000 ml of water, 5.47g of thiourea, 6.2g of piperazine and 10 g of the sodium salt of nitromalonaldehyde (prepared according to Organic Synthesis, Coll, Vol IV p.844) is heated to 70°C in a 2.5l sulphonating vessel. It is stirred for 15 minutes at this temperature. The mixture is allowed to cool and is concentrated in a rotary evaporator under vacuum until crystallization occurs. It is allowed to stand overnight, is filtered and dried under vacuum. 2.3g of product result. The R_f value is 0.69 measured on a thin layer chromatograph having a film of POLYGRAM SIL G/UV 254 and using a solvent of 30 parts methylethylketone, 10 parts of diethylamine and 12 parts of a 25% ammonia solution.

Examples 72-79

Compounds of the formula



in which the symbols are defined in Table 3 below can be prepared from soluble

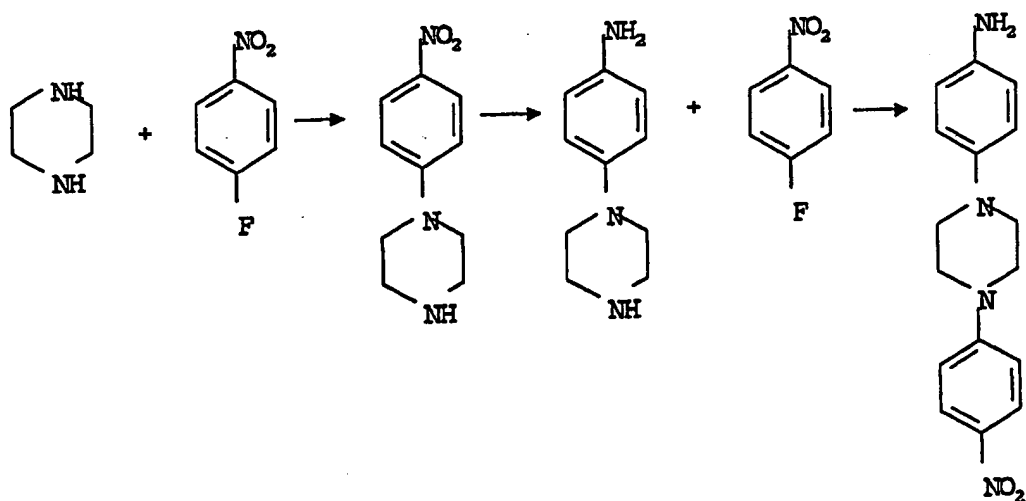
materials by known methods. Rf values are measured according to the method of Example 71.

TABLE 3

Ex. Nr.	Y ₁	Z ₁	Z ₂	R _f
72	-NO ₂	-CH=	-CH=	0.68
73	do	do	-N=	0.68
74	-CHO	do	do	
75	-CH=C(CN) ₂	do	do	
76	-NO ₂	-C(NO ₂)=	-CH=	
77	-CN	-CH=	-N=	
78	-SO ₂ -CH ₂	-CH=	-N=	
79	-SO ₂ -NH ₂	-CH=	-N=	

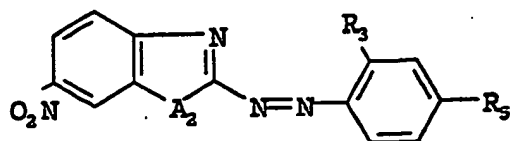
Example 79a

The compound 79a below can be prepared by the following (schematically shown) conventional method.



Examples 80-84

Compounds (i.e. chromophores) of the formula



in which the symbols are shown in Table 4 below can be made from appropriate reactants by a method analogous to that of Example 17 or 18.

TABLE 4

Ex. Nr.	A ₂	R ₃	R ₅	R _f value
80	-S-	-CH ₃	H ₅ C ₂ -N-(CH ₂) ₃ -NH ₂	0.21
81	-S-	H	N-piperazyl	
82	-S-	-CH ₃	H ₅ C-N-(CH ₂) ₃ -NH ₂	
83	-O-	do	do	
84	-S-	H	H ₅ C ₂ -N-(CH ₂) ₃ -NH ₂	

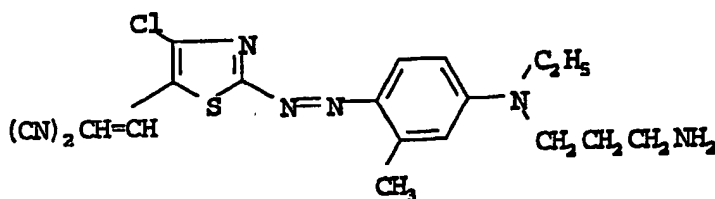
R_f values are measured according to the thin layer chromatography method of Example 17.

Example 85

158g of sulfuric acid (98%) are placed in a 0.5 l sulphonating vessel with stirrer, thermometer and external cooling. 31.5g of 2-amino-4-chloro-5-dicyanovinyl-thioazole (prepared from 2-amino-4-chloro-5-formyl thioazole and malonic acid dinitrile analogously to Example 101 c) of DOS 31 08 077) are added, while stirring well over 30 minutes at 0-5°C. At a temperature of 0-3°C, 48g of a 40% solution of nitrosylsulphonic acid in 98% sulfonic acid are added dropwise over 1 hour. The mixture is then stirred a further 3 hours at 0-3°C.

150g of ice and 17g of 98% sulfonic acid are placed in a 2.5 l sulphonating vessel with stirrer, thermometer and external cooling. 29g of N-ethyl-N-(γ -aminopropyl)-m-toluidine (prepared analogously to the method of Example 18 from N-ethyl-N-(β -cyanoethyl)-m-toluidine) are added. The resulting solution is cooled to 0°C and 1-2g of amidosulphonic acid are added. The above diazonium salt solution is pumped in over one hour, keeping the temperature at 0-5°C by the addition of 500-800g of ice and external cooling. The mixture is allowed to stand for 1-2 hours while stirring and then it is filtered in a vacuum filter G3. The residue is suspended in about 4 l of water, stirred for 30 minutes, filtered and vacuum dried.

To purify the product, it is reacted at room temperature with 400 ml of dimethylformamide and the insoluble parts are filtered off and then it is added to 2.5 liters of chloroform. The precipitated dyestuff is filtered off, and the purification process is repeated. Finally the product is washed with 1000 ml chloroform and dried under vacuum. 15 g of a compound (in ammonium salt form) of the formula

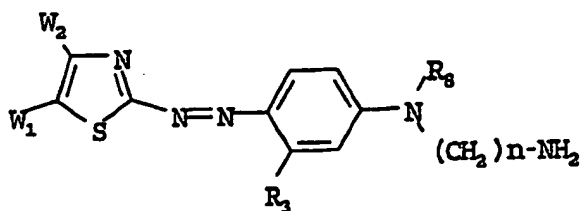


R_f value: 0.14.

Measured according to the thin layer chromatography method of Example 17.

Examples 86-100

Compounds of the formula



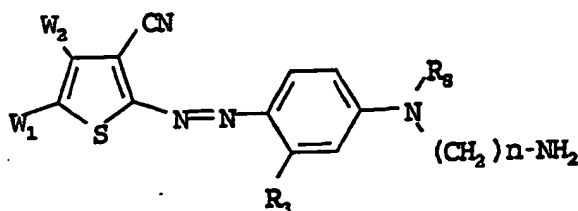
in which the symbols are defined in Table 5 below can be prepared from appropriate reactants by known methods.

TABLE 5

Ex. Nr.	W_1	W_2	R_3	R_8	n	Rf
86	$-\text{CH}=\text{C}(\text{CN})-(\text{COOC}_4\text{H}_9)$	Cl	$-\text{CH}_3$	$-\text{C}_2\text{H}_5$	3	0.15
87	$-\text{CH}=\text{C}(\text{CN})_2$	H	do	do	3	0.01
88	$-\text{NO}_2$	H	H	do	2	0.19
89	$-\text{CH}=\text{C}(\text{CN})_2$	Cl	H	do	2	0.22
90	$-\text{CHO}$	Cl	$-\text{H}$	do	3	0.23
91	$-\text{CH}=\text{CH}-\text{NO}_2$	Cl	$-\text{CH}_3$	do	3	
92	$-\text{CH}=\text{C}(\text{CN})_2$	CH_3	do	do	3	
93	do	C_6H_5	H	do	2	
94	do	Cl	H	$-\text{CH}_3$	2	
95	do	Cl	H	$-\text{C}_2\text{H}_5$	3	0.15
96	$-\text{CH}=\text{C}(\text{CN})-(\text{COOCH}_3)$	Cl	$-\text{CH}_3$	do	3	
97	do	Cl	do	do	3	
98	$-\text{CH}=\text{C}(\text{CN})-(\text{COOCH}_3)$	Cl	do	do	3	
99	$-\text{CH}=\text{C}(\text{COOC}_2\text{H}_5)_2$	Cl	do	do	3	
100	$-\text{C}(\text{CN})=\text{C}(\text{CN})_2$	Cl	do	do	3	

Examples 101-108

Compounds of the formula



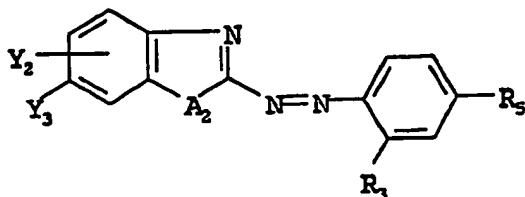
in which the symbols are defined in Table 6 can be prepared by a method analogous to that of Example 85 from suitable reactants.

TABLE 6

Ex. Nr.	W_1	W_2	R_3	R_8	n
101	-CHO	Cl	-CH ₃	-C ₂ H ₅	3
102	do	Cl	H	do	2
103	-CH=C(CN) ₂	Cl	-CH ₃	do	3
104	-CH=C(CN)(COOC ₄ H ₉)	Cl	H	do	2
105	do	Cl	-CH ₃	do	3
106	-CH=C(CN)(COOC ₄ H ₉)	Cl	-CH ₃	do	3
107	-CH=CH ₂ -NO ₂	Cl	-CH ₃	do	3
108	-C(CN)=(CN) ₂	Cl	-CH ₃	do	3

Examples 109-113a

Compounds of the formula



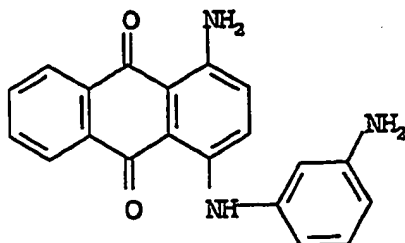
in which the symbols are defined in Table 7 can be prepared from known compounds by standard diazotization and coupling procedures.

TABLE 7

Ex. Nr.	A ₂	Y ₂	Y ₃	R ₃	R ₅	R _f
109	S	Cl	Cl	H	-NH ₂	0.77
110	S	Cl	Cl	-CH ₃	-N(C ₂ H ₅)-(CH ₂) ₃ NH ₂	0.23
111	S	Cl	Cl	H	do	0.23
112	S	H	H	-CH ₃	-N(C ₂ H ₅)-(CH ₂) ₂ NH ₂	
113	O	H	H	do	do	
113a	S	Cl	Cl	H	do	

Example 114

A compound of the formula



can be prepared by desulphonating, by known methods the 2-sulphonic acid derivative.

Example 115

Reaction of poly-(styrene-co-maleic acid anhydride) of Example 1 with the chromophore of Example 18.

A filtered solution of 2.01 g of the chromophore of Example 18 in 50 ml of dimethylformamide is added in drops to a solution of 1.17 g of poly-(styrene co maleic acid anhydride) in 15 ml of dimethylformamide, and the solution is stirred for 2 hours at room temperature. The preparation is filtered and slowly added dropwise to 650 ml of methanol, the precipitated product is filtered off, washed with methanol and dried at 50°/33 mbar.

According to the method described above, the reaction may be carried in 20ml. dimethylformamide as a solvent; before precipitation, the solution of the polymer is diluted with further 20 ml. dimethylformamide, N-methylpyrrolidone or tetrahydrofuran.

The precipitation of the polymer may also be performed in acetic acid ethyl ester.

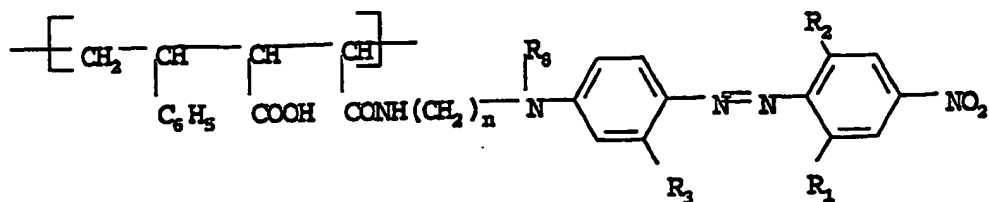
The reaction according to Example 115 may also be carried out in N-methylpyrrolidone as a solvent.

The reaction according to Example 115 may also be performed with the ammonium salt of the dyestuff, with the addition of 2.5 ml. triethylamine in dimethylformamide or in N-methylpyrrolidone.

According to the method described in Example 115, the reaction may also be carried out at temperatures between room temperature and 120°C.

Examples 116-117

Compounds having repeating units of the formula



in which the symbols are defined in Table 8, can be prepared by a method analogous to that of Example 115 from appropriate reactants.

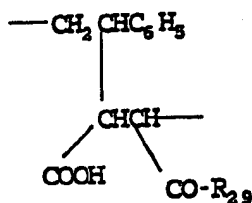
TABLE 8

Ex Nr.	R ₉	R ₃	R ₁	R ₂	n	Mw (backbone) [g/mol]	Chromo- phore* [mol%]	λ _{max} [nm]
116	-CH ₃	H	Cl	H	3		86	516(DMF)
117	-C ₂ H ₅	-CH ₃	Cl	H	3	110000	95	

* Chromophore units per 100 repeating units of the backbone (also in the following tables).

Examples 118-126

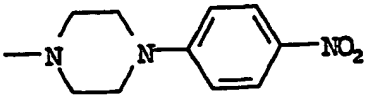
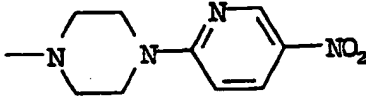
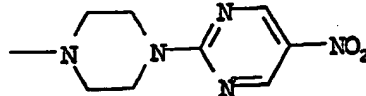
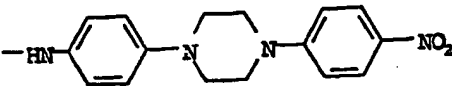
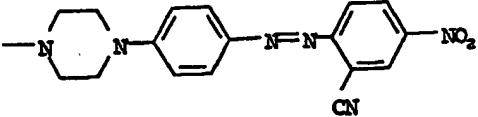
Compounds having repeating units of the formula

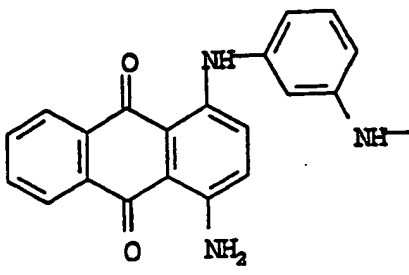


in which R₂₉ is defined in Table 9 can be prepared by a method analogous to that of Example 115 from known compounds.

TABLE 9

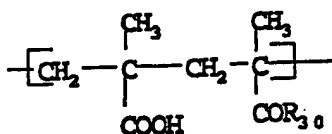
Ex Nr.	R ₂₉	Mw (backbone) [g/mol]	Chromo- phore [mol%]	λ _{max} [nm]
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118			97	393(DMF)
119			91	377(DMF)
120			91	352(DMF)
121			79	391(DMF)
122			98	523(DMF)
123	$\text{-HN-CH}_2\text{-CH}_2\text{-CH}_2\text{-N(C}_6\text{H}_5\text{)CH}_3$			

124		70000	75	617, 579 (DMF)
125	do	70000	45	618, 580 (DMF)
126	do	145000	77	

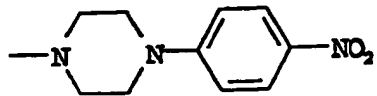
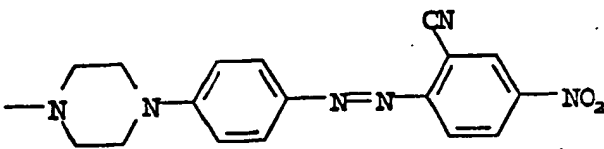
Examples 127-128

By modifying the procedure of Example 115 to start with insoluble poly(methacrylic acid anhydride prepared in Example 6 in suspension, compounds having repeating units of the formula



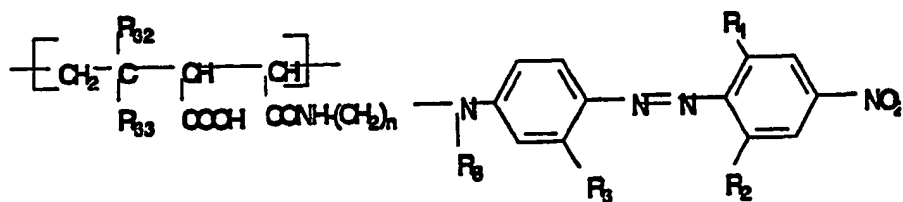
in which R_{30} is defined in Table 10 below can be prepared.

TABLE 10

Ex. Nr.	R ₃₀	Chromophore [mol%]	λ _{max} [nm]
127		70	
128		54	525(DMF)

Examples 129-132

Compounds having recurring units of the formula



in which the symbols are defined in Table 11 below can be prepared by a process analogous to that of Example 115.

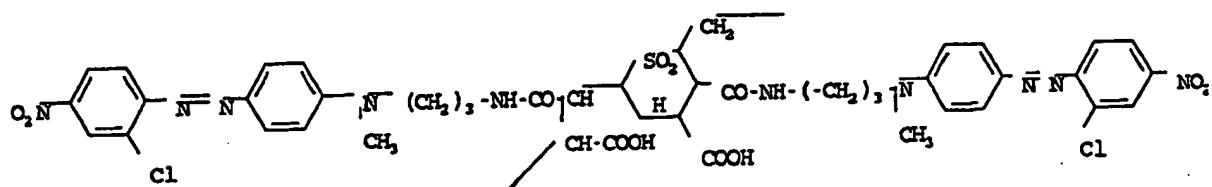
TABLE 11

Ex. Nr.	R ₃	R ₃	R ₁	R ₂	n	R ₃₂	R ₃₃	Chromophore	λ_{\max}
129	-CH ₃	H	Cl	H	3	-OC ₂ H ₅	H	72	
130	do	H	Cl	H	3	H	H	79	
131	C ₂ H ₅	-CH ₃	CN	H	3	-C ₆ H ₅ -p-OH	H	84	553(DMF)
132	do	do	Cl	H	3	do	H	92	

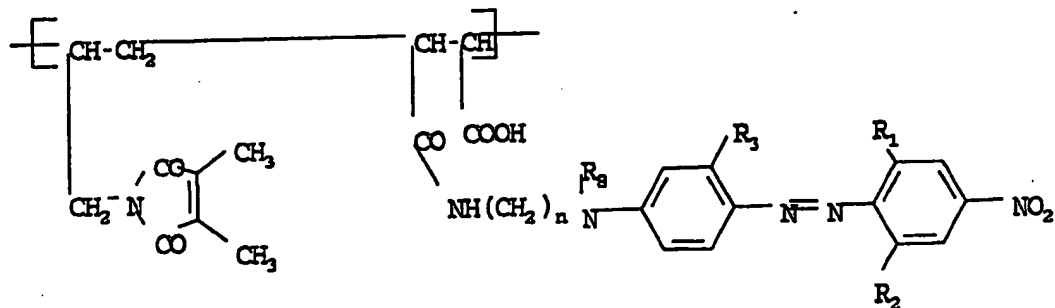
Examples 133-135

Similar compounds of the formulae

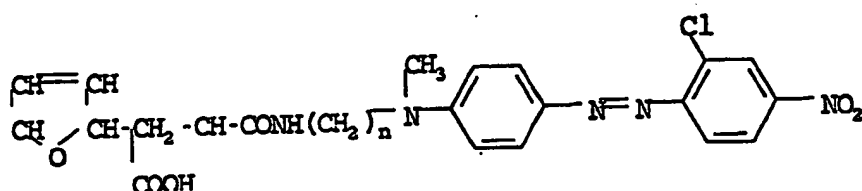
Formula 12



Formula 13



Formula 14



in which the symbols of Examples 133-135 are defined in Table 12 below can be prepared from appropriate reactants.

Table 12

Ex. Nr.	R ₂	R ₃	R ₁	R ₂	n	Formula	Chromo- phore	λ _{max} [nm]
133	-CH ₃	H	Cl	H	3	12		
134	-C ₂ H ₅	-CH ₃	-NO ₂	Br	3	13	41	
135	-CH ₃	H	Cl	H	3	14	75	

Example 136

Reaction of the polyamide acid of Example 115 and ring closure to form the imide.

0.66ml of acetic anhydride and, optionally, trimethylchlorosilane are added to the reaction mixture of Example 115. This mixture is stirred for 2 hours at 120°C. After cooling, the solution is filtered and is slowly added dropwise to a mixture of 700 ml of methanol and 70 mls of water. The precipitated product is filtered and dried at 50°C/25 torr.

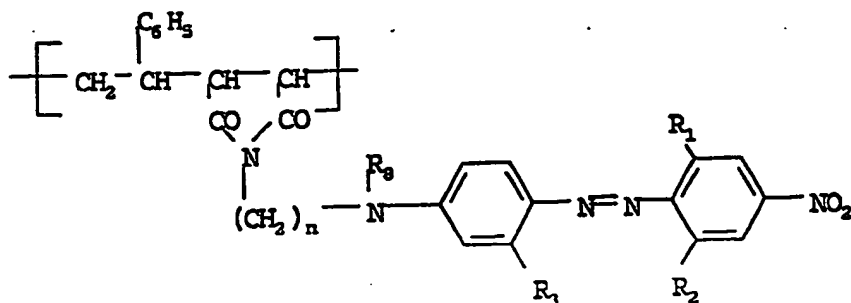
The polymer may also be prepared with oxalylchloride in tetrahydrofuran in the place

of acetic anhydride.

According to the method described in Examples 115 and 136, the reaction may also be carried out by addition of trimethylchlorosilane and trimethylamine to the dyestuff, followed by adding this mixture to a solution of the polymer.

Example 137-159

Compounds having recurring units of the formula



in which the symbols are defined in Table 13 can be prepared from appropriate reactants by a method analogous to that of Example 115 or Example 133.

TABLE 13

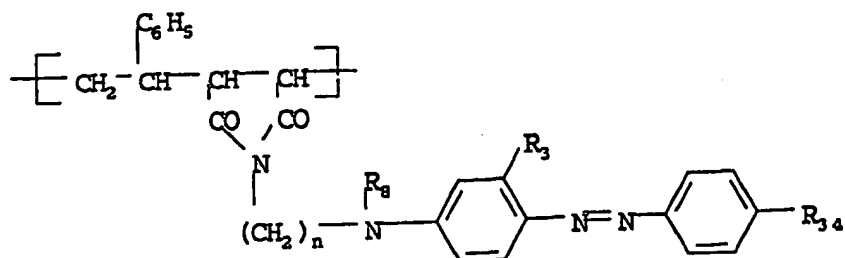
Ex Nr.	R ₃	R ₃	R ₁	R ₂	n	Mw (Backb) [g/mol]	Chr omo- phor [mol %]	Tg[° C]	λ _{max} . [nm]
137	C ₂ H ₅	-CH ₃	H	H	3		68	161	
138	do	do	H	H	3	110000	63		
139	do	do	H	H	3	110000	46		
140	do	do	H	H	3	70000	94	140	504(DMF)
141	do	do	H	H	3		90	137	494 (CH ₂ Cl ₂)
142	do	do	H	H	3	70000	58		507(DMF)
143	do	do	Cl	H	3		61	164	530(DMF)
144	do	do	Cl	H	3		82	148	
145	do	do	Cl	H	3	110000	76		

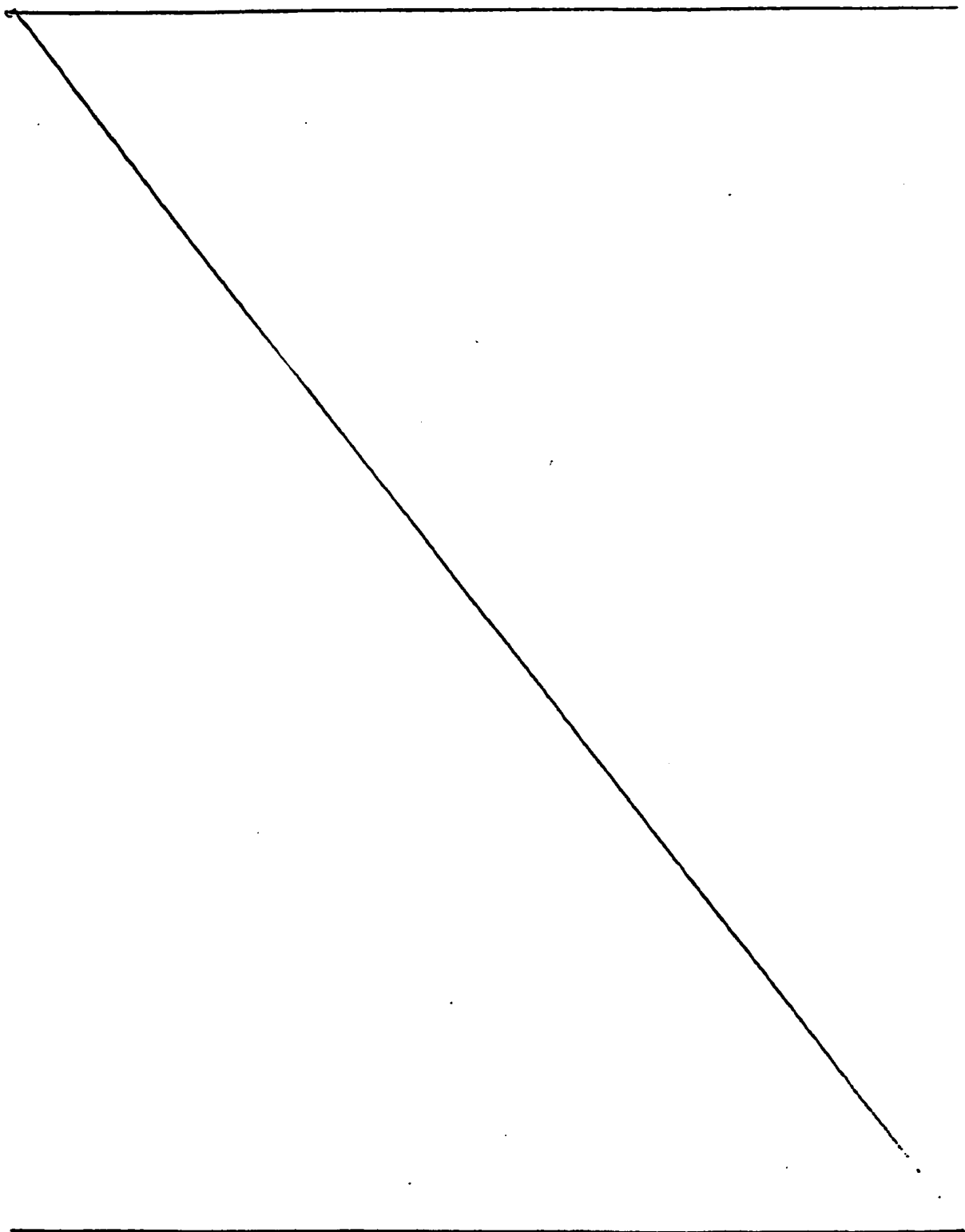
Ex Nr.	R ₃	R ₃	R ₁	R ₂	n	Mw (Backb) [g/mol]	Chr omo- phor [mol %]	Tg[° C]	λ _{max} . [nm]
146	do	do	Cl	H	3	110000	80	149	
147	do	do	Cl	H	3		85		
148	do	do	Cl	H	3	110000	89		
149	-CH ₃	H	H	H	2	70000	92	170	468(CH ₂ Cl ₂)
150	do	H	H	H	2	70000	81	177	
151	do	H	H	H	2	70000	58	186	
152	do	H	H	H	2	4000000	58		
153	do	H	H	H	2	4000000	56		
154	-C ₂ H ₅	H	H	H	2	110000	86	172	481(DMF)
155	do	H	H	H	2	70000	54	186	485(DMF)
156	do	H	H	H	2	70000	36	201	486(DMF)
157	-CH ₃	H	Cl	H	3	110000	80		508(DMF)
158	-CH ₂ C ₆ H ₅	-CH ₃	Cl	H	3		81	139	506(DMF)
159	-C ₂ H ₅	do	NO ₂	Br	3		81		

Examples 160-170

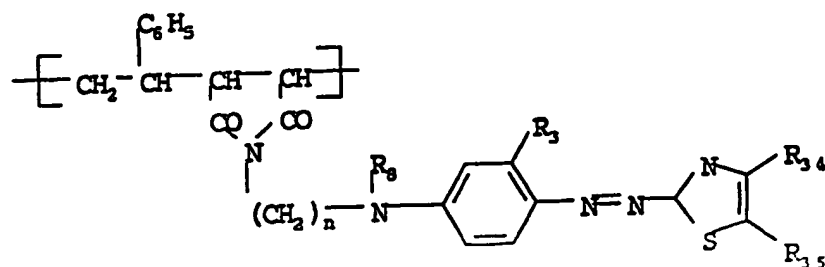
Compounds containing recurring units of formula 16 or 17

Formula 16





Formula 17



in which the symbols and the formulae to which the Examples refer are defined in Table 14 below can be prepared from appropriate reactants by known methods.

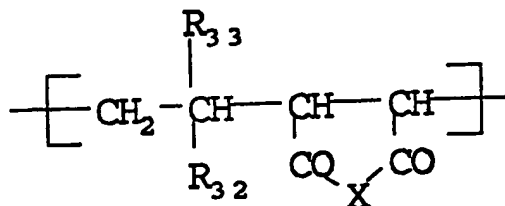
TABLE 14

Ex Nr.	R ₈	R ₃	R ₃₄	R ₃₅	Formula of Examples	n
160	-C ₂ H ₅	-CH ₃	-CHO		16	3
161	do	H	do		16	2
162	do	H	CH=C(CN) ₂		16	3
163	do	H	do		16	2
164	do	H	Cl	-CHO	17	3
165	do	H	Cl	-CHO	17	3
166	do	H	Cl	-CHO	17	2
167	do	H	Cl	CH=C(CN) ₂	17	3
168	do	H	H	do	17	3
169	do	H	Cl	do	17	2

170	do	H	H	do	17	2
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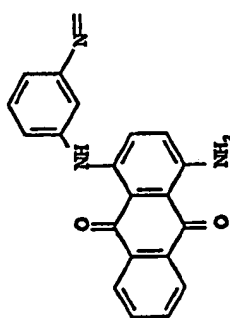
Examples 171-181

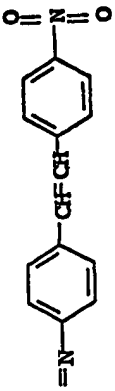
Compounds containing recurring units of formula 18

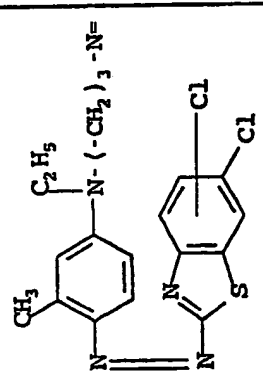


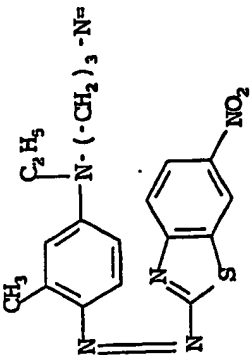
in which the symbols are defined in Table 15 below can be prepared from suitable reactants.

TABLE 15

Ex.	X	R ₃₂	R ₃₃	M _w	Chromo- phore	mp	λ _{max}
171	$\text{=N-(CH}_2)_3\text{-N-CH}_3$ C_6H_5	C_6H_5	H		68	131	
172	do	H	$\text{-C}_6\text{H}_4\text{-m-CHO}$				
173		C_6H_5	H	70000	70		

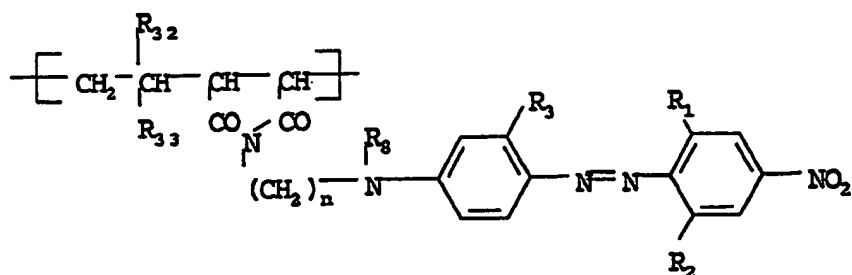
Ex.	X	R ₃₂	R ₃₃	Mw	Chromo- phore	mp	λ _{max}
174	do	do	H	70000	31		
175	do	-CH ₃	H	145000	70		
176		H	H	245000	78		361(DMF)
177	do	C ₆ H ₅	H		43		

Ex.	X	R ₃₂	R ₃₃	Mw	Chromo- phore	mp	λ_{max}
178		do	H		72		525(DMF)
179	do	do	H		42		

Ex.	X	R ₃₂	R ₃₃	Mw	Chromo- phore	mp	λ _{max.}
180		do	H		64		553(DMF)
181	do	do	H		39		

Examples 182-194

Compounds containing recurring units of the formula



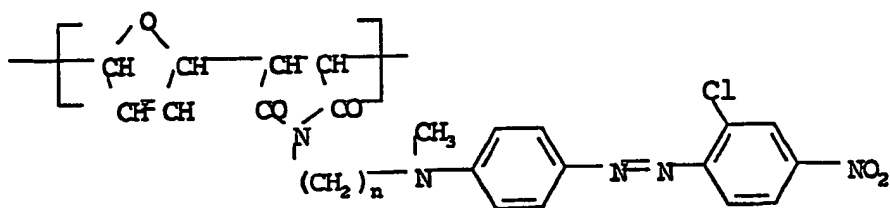
in which the symbols are defined in Table 16 can be prepared analogously to the method of Example 115 from appropriate reactants.

TABLE 16

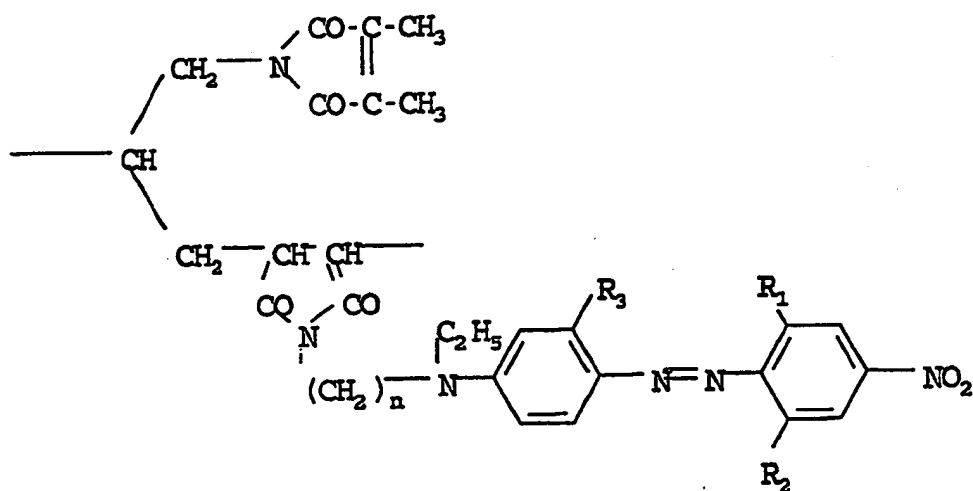
Ex. Nr.	R ₈	R ₃	R ₁	R ₂	n	R ₃₂	R ₃₃	M _w (Back) [g/mol]	Chrom- ophore [mol %]	Tg[°C]	λ _{max} [nm]
182	-CH ₃	H	Cl	H	3	-OC ₂ H ₅	H		80	135	499(DMF)
183	do	H	Cl	H	3	H	H	245000	71	113	508(DMF)
184	-C ₂ H ₅	-CH ₃	Cl	H	3	-CH ₃	H	145000	79	137	
185	do	do	Cl	H	3	do	-CH ₃	225000	68	140	
186	do	do	Cl	H	3	-C ₆ H ₅	do		81	152	
187	do	do	H	H	3	do	do	38000	93	137	497(CH ₂ Cl ₂)
188	do	do	H	H	3	do	do	38000	90	142	496(CH ₂ Cl ₂)
189	do	do	H	H	3	do	do	38000		147	
190	-CH ₃	H	H	H	2	do	do	38000	88	178	471(CH ₂ Cl ₂)
191	do	H	H	H	2	do	do	38000	80	185	
192	do	H	H	H	2	do	do	38000	57	192	
193	do	H	H	H	2	-CH ₃	H	145000	88	160	477(DMF)
194	-C ₂ H ₅	H	Cl	H	3	-C ₆ H ₅ -p-OH	H		75		

Compounds containing recurring units of formula 20 to 24

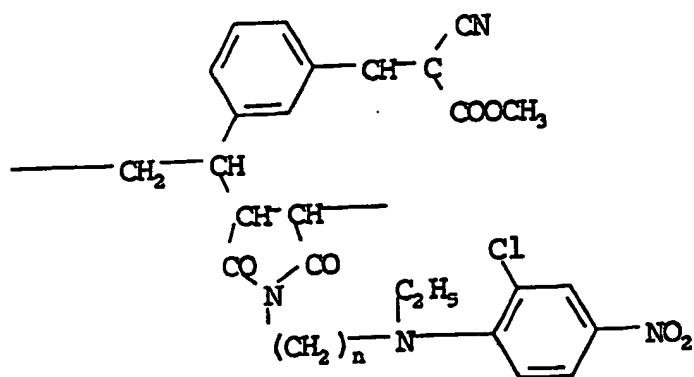
Formula 20



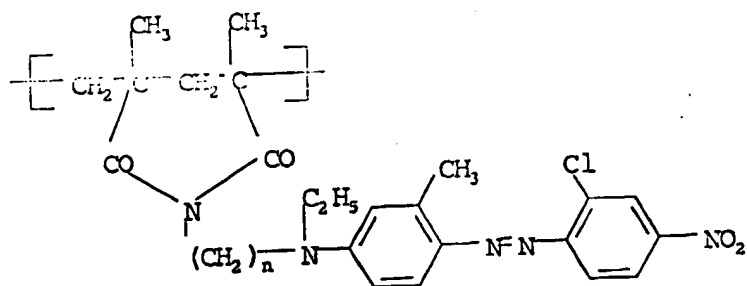
Formula 21



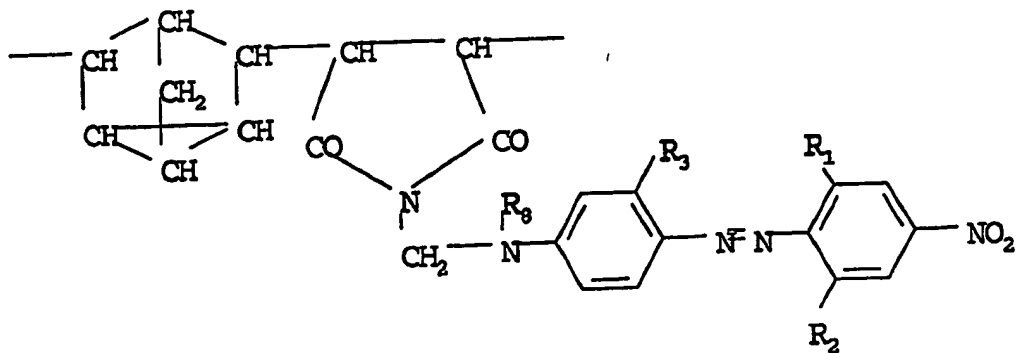
Formula 22



Formula 23



Formula 24



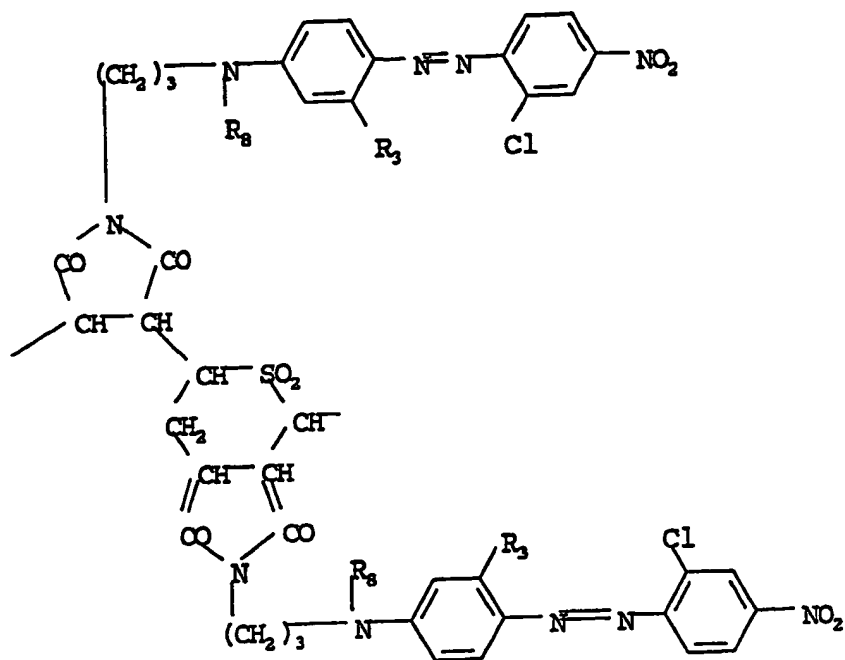
in which the symbols are defined in Table 17 can be made from appropriate reactants.

TABLE 17

Ex. Nr.	R ₈	R ₃	R ₁	R ₂	n	Form	Chrom- ophore [mol]	Tg[°C]	λ_{\max} [nm]
195					3	20	90		497(DMF)
196	-C ₂ H ₅	-CH ₃	NO ₂	Br	3	21	20		575 (DMSO)
197	do	do	Cl	H	3	21	50		518 (CH ₂ Cl ₂)
198					3	22	66	146	516, 300 (THF)
199					3	23	81	132	529(DMF)
200	do	do	H	H	3	24	97	151	503(DMF)
201	-CH ₃	H	H	H	2	24	96	180	

Examples 202-203

Compounds of formula 25



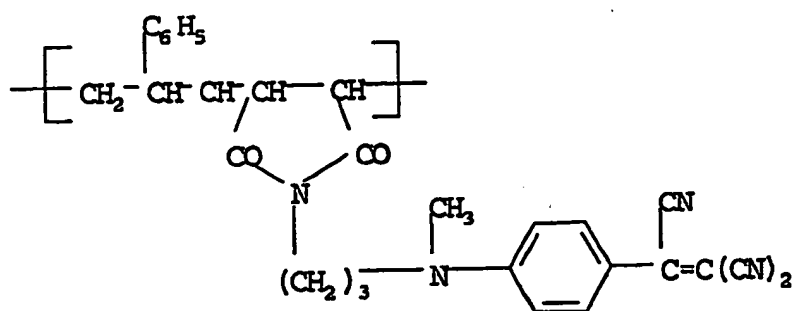
in which the symbols are defined in Table 18 below can be prepared from appropriate reactants by a method analogous to that of Examples 115 or 136.

TABLE 18

Ex. Nr.	R ₁	R ₂	Chromo- phore [mol %]	Tg[°C]	λ _{max} [nm]
202	-C ₂ H ₅	-CH ₃	43	151	
203	-CH ₃	H			523(DMSO)

Example 204

A compound containing recurring units of formula 26

Formula 26

can be prepared as follows:

0.15g of tetracyanoethylene are added to a solution of 0.42g of the copolymer of Example 171 in 5ml of N-methylpyrrolidene. The dark red reaction solution is stirred for 5 hours at room temperature, it is then diluted with 2ml of N-methylpyrrolidene, filtered and slowly added dropwise to 200ml of acetic acid ethyl ester. The precipitated copolymer is filtered and dried at 30°C and 25 torr.

UV: $\lambda_{\text{max}} = 527\text{nm}$ (NMP)

Application Example 205

1g of the polymer of Example 141 is dissolved over 4 hours at room temperature in 9g of a mixture of 8.1g of cyclohexanone and 0.9g of N-methylpyrrolidone. To remove dust particles, the solution is filtered through a PTFE filter having an average pore size of 0.2 μ m.

A glass plate having a size 50x50 mm is cleaned as follows: it is treated with a concentrated soap solution in an ultrasonic bath for about 1 hour, washing with sequentially distilled water, acetone and distilled water again and finally drying in a vacuum drying cupboard for about 12 hours at 80°C.

In a dust-free atmosphere, in a spin coating apparatus the abovementioned polymer solution is spun on to the glass plate at 2400 revs/min. over 50 sec. Finally this is dried for about 20 hours at 70°C, 150°C and 170°C.

A homogenous film with good optical properties results. The thickness of the film is 0.4-0.5 μ m (measured on a Alpha Step from Tencor)

The film is polarized in a Corona Poling machine at 140-150°C at about 5 kVolt over 30 mins.

The poling procedure is carried out by SHG measurements according to the maker fringe methods at 1064nm as described for example by M.A. Mortazavi et al in J. Opt. Soc. Am. B, 6(4) 741 (1989).

After achieving the maximum SHG signals the plates are cooled to room temperature by means of the activated electric field.

The following values for the Non-Linear Optics (NLO) coefficients result: $d_{31}=360$ pm/V (1064nm, resonance increase).

Application Examples 206-209

Analogously to Application Example 205, polymers defined in Table 19 can be applied by spin coating at a thickness of 0.4-0.5 μ m. The optimal poling temperature as well as the d 31 are given in Table 19. In Example 209 the glass plate used was Indium Tin Oxide (ITO) glass 26x75mm from Balzer. Spinning rate was 3800 revs/min. over 50 sec. Film thickness was 1.6-1.9 μ m.

TABLE 19

Ex. Nr.	Polymer from Example	Optimal poling temp.	d31** (pm/V)
206	146	150-160°C	280
207	149	170-180°C	361
208	180	170-200°C	90
209	154	170-180°C	78 (1313nm)

** except Example 209 where it is d 33.

The polymer fiber when poled shows good long stability.

Application Example 210

The following polymer solutions are formed

- 1g of the polymer of Example 138 in a mixture of 3.6g of cyclohexonane and 0.4g of N-methylpyrrolidone. (Polymer a)
- 2g of the polymer of Example 146 in a mixture of 5.4g of cyclohexonane and 0.6g of N-methylpyrrolidone. (Polymer b)
- 2g of the polymer of Example 1 in a mixture of 7.2g of cyclohexonane and 0.8g of N-methylpyrrolidone. (Polymer c)

To remove dust particles, the solutions are passed through a Teflon filter having a

average size of $0.2\mu\text{m}$.

Production of polymer layers

- a) A silicon wafer is cut to the size of $20\times 20\text{mm}$ and purification is carried out as per Example 205 (for glass plates). Under a dust-free atmosphere, the polymer a) is coated on to the silicon wafer in a spin coating apparatus at 3800 rev/min . over 50 seconds. The layer is then dried in a drying cupboard sequentially for 20 hours at the following temperatures 70°C , 150°C and 170°C . The thickness of the layer of polymer a) is $1.65\mu\text{m}$.
- b) A second layer of polymer b) is deposited on top of polymer layer a) to form a double layer by means of a spin coating, as above, at 3400 revs/min for 50 seconds. Drying is carried out, as above. The thickness of the double layer a) and b) is $4.45\mu\text{m}$.
- c) Polymer c) deposited on top of polymer fiber a) and b). A third fiber of polymer c) is deposited on top of the double fiber a) by spin coating as described above at 5700 revs/min for 50 seconds. Drying is performed as described above. The thickness of the three layers is $6.45\mu\text{m}$.

Two parallel grooves spaced 1 cm. apart are etched into the silicon wafer. One of the grooves is coupled to a laser beam having a wavelength of 1064 nm , and the other groove with a IR camera and monitor to measure the light being emitted. The polymer layers show excellent wave guiding properties.

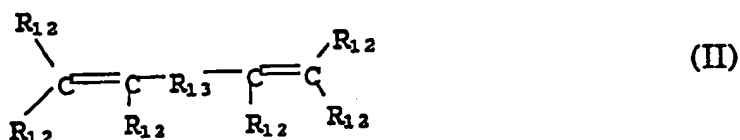
Example 211

Electrooptical devices, as described in SPIE Proceeding 1337, 215 (1990) can be prepared using the three layer polymer fiber produced in Example 210.

Claims

1. A polymer having non-linear optical properties, comprising a polymeric backbone a) (hereinafter defined as polymer backbone a) and at least one chromophore b) (hereinafter defined as chromophore b) attached thereto by means of a bridging moiety (hereinafter defined as bridging group c); the bridging group so constituted that the chain of linking atoms (hereinafter defined as chain d) thereof does not contain an ester linkage.
2. A polymer according to claim 1 in which the chain d) does not contain a urea group (-NH-CO-NH-).
3. A polymer according to claim 1 or claim 2 in which the bridging group c) contains an imide, isoimide or imide group, provided the chain d) does not contain an ester-amide group.
4. A polymer according to any one of the preceding claims in which the bridging group c) contains an amino alkyl imido group, the amino being bound to the chromophore and the imido group being bound to the polymer chain.
5. A polymer according to any one of the preceding claims in which the glass transition temperature (T_g) of the polymer is from 120-250°C, more preferably 135-210°C.
6. A polymer according to any one of the preceding claims in which the basis polymer for forming the polymer backbone a) (hereinafter defined as the "basis" polymer) is a homo-, co- or ter-polymer derived from monomeric compounds having one or more groups capable of condensation and/or polymerization.
7. A polymer according to claim 6 in which the monomeric compounds are preferably selected from aliphatic or cyclic anhydrides or imides, for example,

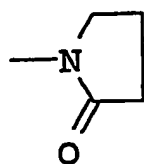
maleic anhydride, maleic acid imide, methacrylic acid anhydride, itaconic acid anhydride or a citraconic acid anhydride which, if copolymers form, react with vinylic compounds such as thiophene, dihydrofurane, dihydropyrane, cyclohexene, indole and N-alkylindole compounds of the formula



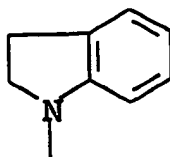
in which

R_{10} , is selected from hydrogen, chloro and C_{1-6} alkyl; and

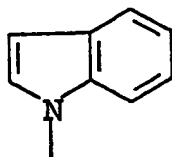
R_{10a} is selected from hydrogen, chloro, C_{1-6} alkyl, phenyl, C_{1-6} alkoxy, C_{1-5} alkyl carbonyloxy, C_{1-5} alkoxy-methyl, C_{1-5} alkylcarbonyloxymethyl, C_{1-4} alkyloxy-carbonyl and a group of formulae a) to f)



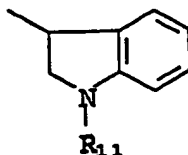
(a)



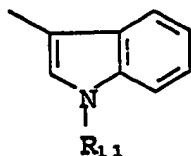
(b)



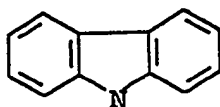
(c)



(d)



(e)



(f)

where

- R_{11} is hydrogen or C_{1-6} alkyl;
 each R_{12} independently is hydrogen or methyl;
 R_{13} is a bridging group, preferably selected from $-O-$, $-S-$, $-SO_2-$, $-CH_2-O-$, $-CH_2-O-CH_2-$, $-CO-$, $-[C(R_{14})_2]-$ or $-[Si(R_{14})_2]-$ where each R_{14} independently is selected from hydrogen, methyl and C_{4-6} cycloalkyl or both groups R_{14} form an omega C_{4-6} cycloalkylene group;
 R_{15} is $-CH_2-$;
 each R_{16} and R_{17} independently is selected from hydrogen, $-CH=CH_2$, $-CH=CHCH_3-$, $-C(CH_3)=CH_2$, $-CHO$ or $-COCH_3$; or
 both groups R_{16} together form a group $=CH_2$ or $=CH-CH_3$ and both groups R_{17} are hydrogen;
 or one group R_{16} and one group R_{17} form a bridge of the formula $-CH_2-CH=CH-$ or $-CO-O-CO-$ and the other group R_{16} and the other group R_{17} are hydrogen;
 R_{18} is hydroxy, carboxy, formyl or a group of the formula
- $$\begin{array}{c} \text{---CH=C---CO---R}_{20} \\ | \\ \text{R}_{19} \end{array}$$

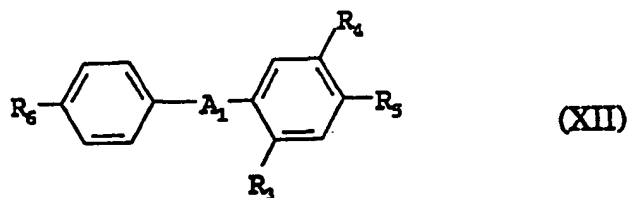
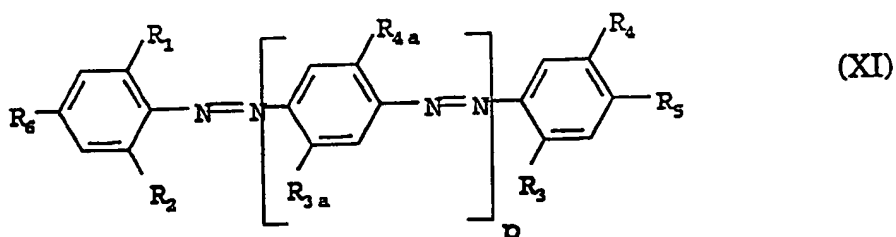
- where R_{19} is hydrogen, methyl, ethyl or cyano; and R_{20} is hydrogen, hydroxy or C_{1-4} alkoxy;
 each R_{18a} is hydrogen, fluoro or chloro; and
 each R_{21} independently is halogen, preferably chloro or bromo or C_{1-4} alkyl and R_{22} is vinyl or alkyl.

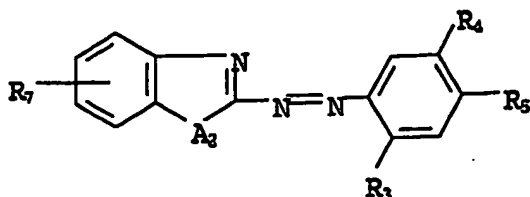
8. A polymer according to claim 6 in which the basis polymers are the reaction products of
- i) an aliphatic or cyclic anhydride or imide, preferably maleic anhydride,

maleic acid imide, methacrylic acid anhydride, itaconic acid anhydride or citraconic acid anhydride (hereinafter component i); with

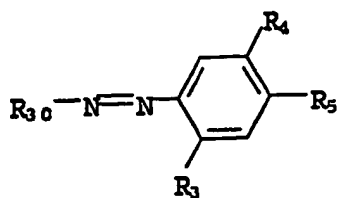
- ii) a compound selected from thiophene, 2,3- or 3,4 dihydrofurane, 2,3-dihydropyran, cyclohexene, indene, indole, N-C₁₋₄alkylindole and a compound of formula I to V defined in claim 7 (hereinafter component ii) .

9. A polymer according to claim 5 in which the ratio of component i) to component ii) is 1:1 to 1:10, except when component i) is a cyclic anhydride and component ii) is a compound of formula II in which case the ratio is 3:1 to 1:1.
10. A polymer according to anyone of the preceding claims in which the chromophore b) is derived from chromophore-bearing compounds with non-linear optical properties of formula XI-XV





(XIV)



(XV)

in which

R_1 is hydrogen, halogen, carboxyl, cyano or rhodan;

R_2 is hydrogen, halogen, cyano, carbonyl or nitro;

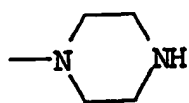
R_3 is hydrogen, methyl, ethyl, methoxy, ethoxy, amino- C_{1-2} alkyl or C_{1-2} alkylcarbonyl amino;

R_{3a} is hydrogen, methyl, ethyl, methoxy or ethoxy

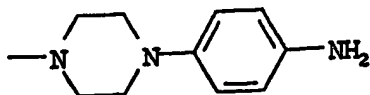
R_4 is hydrogen, methoxy or ethoxy;

R_{4a} is hydrogen, methoxy or ethoxy;

R_5 is a group of the formula $-NH_2$, $-N(R_6)-(CH_2)_n-NH_2$;

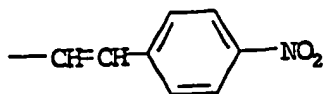


or



and when R_3 is C_{1-2} alkyl amino, R_5 may additionally be $di(C_{1-4}$ alkyl) amino;

R_6 is cyano, nitro, C_{1-2} alkylsulphonyl, aminosulphonyl, dicyanovinyl, tricyanovinyl, $di(C_{1-4}$ alkoxycarbonyl) vinyl of a group of the formula $-C(C_{1-4}\text{-alkyl})=C(CN)_2$, $-CH=CH-NO_2$, $-CH=C(CN)-CO-O-C_{1-4}$ alkyl, or



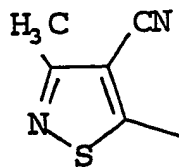
R_7 is hydrogen or nitro;

R_8 is hydrogen, C_{1-4} alkyl, benzyl or C_{1-2} alkoxycarbonyloxy- C_{2-3} alkyl;

A_1 is a direct bond, $-\text{CH}=\text{CH}-$, $-\text{N}=\text{CH}-$ or $-\text{CH}=\text{N}-$;

A_2 is $-\text{S}-$ or $-\text{O}-$;

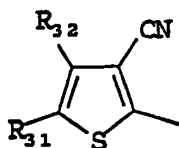
R_{30} is a group of the formula a), b) or c)



a)



b)



c)

where

R_{31} is tricyanovinyl, $-\text{NO}_2$, $-\text{CHO}$, $-\text{CH}=\text{C}(\text{CN})_2$, $-\text{CH}=\text{CH}-\text{NO}_2$, $-\text{CH}=\text{C}(\text{CN})(\text{COOC}_{1-4}\text{alkyl})_2$ or $\text{CH}=\text{C}(\text{COOC}_{1-4}\text{alkyl})_2$

R_{32} is hydrogen, chloro, C_{1-4} alkyl or phenyl;

Y_1 is nitro, formyl, cyano, C_{1-2} alkylsulphonyl, tricyanovinyl or dicyanovinyl;

$-\text{Z}_1=$ is $-\text{N}=$, $=\text{CH}-$ or $=\text{C}(\text{NO}_2)-$;

$-Z_2=$ is $=N-$, $=CH-$ or $=C(NO_2)-$;

p is 0, 1 or 2; and

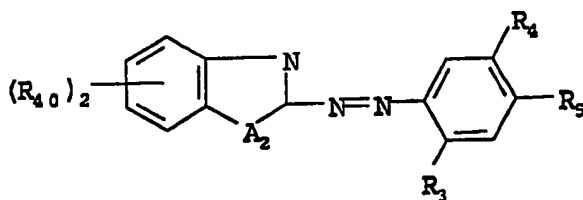
n is 0 or 1 to 9

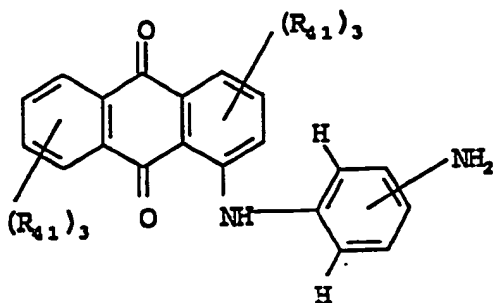
11. A optical device capable of acting as a wave guide for lower light of differing wavelengths containing a polymer according to any one of the preceding claims.

12. An optical device comprising

- a) a top buffer being a layer of polymer a) as defined above containing no non-linear optical (NLO) chromophore, a minor amount of NLO chromophore or non-NLO chromophore;
- b) a main layer being a layer of a polymer according to any one of the preceding claims combining 10-100% NLO chromophore; and
- c) a bottom buffer, being a layer of polymer a) containing no NLO chromophore, a minor amount of NLO chromophore (e.g. from 1-10%) or non-NLO chromophore.

13. A device according to claim 12 in which the non-non-linear optical chromophores (non-NLO chromophores) are those of formula VI and VII





in which A_2 , R_3 , R_4 and R_5 are defined in claim 10;

each R_{40} independently is selected from hydrogen, fluoro, chloro, bromo, methyl and methoxy; and

each R_{41} independently is selected from hydrogen, chloro, bromo, amino, mono- or di C_{1-4} alkylamino C_{1-4} alkoxy and hydroxy.

14. A polymer with non-linear optical properties substantially as herein described with reference to any one of the Examples.
15. A device containing a polymer with non-linear optical properties substantially as herein described with reference to any one of the Examples.

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Patents Act 1977

Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

GB 9308327.7

Relevant Technical fields

(i) UK CI (Edition L) C3P - PDA, PDM, PDW
C3J - JAT, JCF

(ii) Int CI (Edition 5) C08F

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Search Examiner

M J PRICE

Date of Search

23 AUGUST 1993

Documents considered relevant following a search in respect of claims

1-15

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X, P	GB A 2255336	(SANDOZ)	
X, P	EP 0514732	(ALCATEL)	
X	EP 0469941	(THOMSON)	
X	WO 91/03001	(MERCK)	
X	WO 89/08686	(MERCK)	
X	US 5064264	(IBM)	
X	US 4935292	(NORTHWESTERN)	
X	US 4611890	(RESEARCH)	

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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